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ALUMINIUM RECOVERY FROM MSWI BOTTOM ASH

Doctoral Dissertation of:
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A Marco, compagno di vita,

e alla nostra principessa che porto in grembo.

Ringrazio innanzitutto Mario per la grande fiducia che mi ha sempre dimostrato e per gli utili suggerimenti che mi ha dato sull'impostazione del lavoro.

Ringrazio poi Lucia, Simone, Alida e Federica, che mi hanno sopportato in questi anni, e ovviamente Giovanna, che ha condiviso con me questo percorso.

Ringrazio poi CiAl e EAA per il supporto economico, e non solo, senza il quale tale lavoro non sarebbe esistito. Un ringrazio particolare va anche al Prof. Buekens, per il puntuale lavoro di revisione effettuato su gran parte del mio lavoro, e al Dott. Pruvost, per tutte le informazioni e suggerimenti che mi ha fornito.

Un particolare ringraziamento a Alessandro, Alessandra e Amed di Carlo Vedani Metalli.

Infine, il ringrazio più grande alla mia famiglia e a tutti i miei amici.

ABSTRACT

Recovering aluminium and other non-ferrous metals from waste incineration bottom ash has become a common practice in the last decades. The concentration of these metals in the bottom ash can be higher than that in the ore, making their recovery advantageous from an economical point of view. In addition, significant environmental benefits are associated to their recycling, and their separation is crucial in view of the recovery of the inert fraction of the bottom ash.

Despite metals recovery is a common practice, the correct design of the treatment plant is a hard task, since it requires to know how much aluminium is in the ash and what are its main characteristics, in terms of dimensional classification of the lumps and of their quality, expressed by the oxidation level and the presence of other non-ferrous metals.

During this research project, three areas regarding aluminium recovery from the bottom ash were explored:

- The aluminium behaviour in waste-to-energy furnaces. Aluminium mass balance in waste-to-energy (WTE) plants was experimentally investigated, allowing to estimate the actual amount of aluminium present in the bottom ash in the metallic form, i.e. its recoverable form;
- The recovery of aluminium from the bottom ash fine fraction (< 5 mm);
- The perspective for aluminium recovery from bottom ash in Italy in the next 10-20 years.

The estimation of the aluminium mass balance in the furnace of

waste-to-energy plants and of its partitioning in the residues of the combustion process is fundamental to assess the actual amount of aluminium that can be recovered from the bottom ash. In fact, current technologies are able to recover only the aluminium fragments bigger than 1 mm. In addition, during the combustion process, the scraps contained in the waste undergo degradation and oxidation processes that determine a loss of their recoverable mass from the bottom ash. Thus, the knowledge of the oxidation level of the aluminium in the combustion residues is another necessary information.

The extent of the fragmentation and oxidation processes that take place during combustion is strictly related to the structure and the mechanical properties of the material. The experimental investigation conducted within the research project in two full-scale WTE plants shows that the recovery of aluminium from the incineration residues increases proportionally to aluminium thickness in the tested Al input raw materials, as illustrated in Figure A. About 81% of the aluminium in the cans can be recovered from the bottom ash and then recycled as secondary aluminium, but this amount decreases to 51% when trays are considered, 27% for a mix of aluminium and poly-laminated foils and 47% for paper-laminated foils. Foils (Al thickness 10-42 μm) and trays (50 μm) are characterised by lower aluminium recovery yields if compared with beverage cans (90-250 μm), due to a stronger fragmentation on the combustion grate and thus the formation of smaller lumps that are lost within the fine fractions. These values also suggest that the paper used in the paper-laminated foil improves the mechanical strength of the aluminium foil.

In the residual waste, aluminium can be present as packaging or as other materials (like pots, for instance). The amount of aluminium recoverable from the bottom ash is therefore influenced by the waste composition and, thus, by the efficiency of the separated collection applied upstream within the waste management system. Considering the typical composition of the unsorted waste in Northern Italy, only 26-37% of the Al fed to the furnace of the incineration plant can be recovered from the bottom ash. This corresponds to an amount of secondary aluminium potentially producible equal to about 21-23% of the aluminium fed to the furnace, as illustrated in Figure A. These values refer to a situation where most of the aluminium in the residual waste concentrates in the fine fraction of the bottom ash (< 1 mm) and cannot be recovered, since it consists mainly of flexible packaging like the foil. Where the separated collection of waste is less efficient, the amount of aluminium in the residual waste can be higher and also its composition can be different, with a prevailing presence of rigid packaging materials. This may result in a greater amount of aluminium potentially recoverable from the ash.

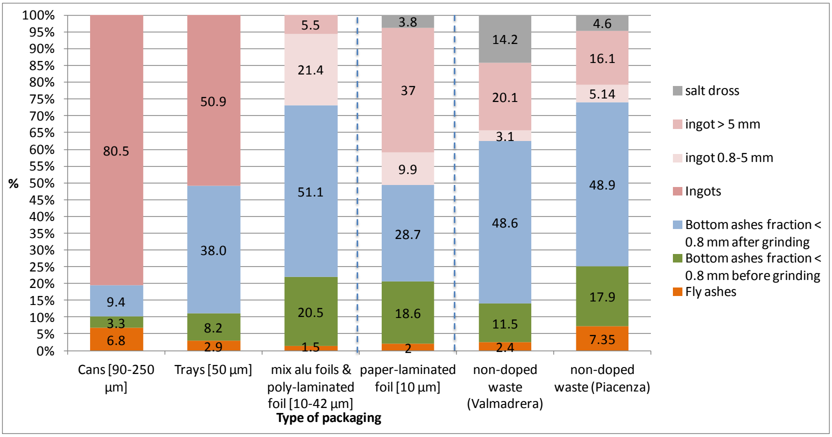

Figure A. Partitioning of total Al in the residue of the incineration process for 4 different types of packaging material and for the mixed aluminium in the URW (non-doped sample).

Aluminium recovery from the bottom ash is particularly difficult when the lumps produced during the combustion process are smaller than 5 mm. In fact, the standard Eddy current separators (ECS) for non-ferrous metals recovery usually installed in the plants, have a good separation efficiency only for lumps bigger than 4-5 mm. The analysis of the bottom ash < 4 mm sampled in a Swedish WTE bottom ash treatment plant showed that only 3% of the total aluminium in the ash, corresponding to about 21% of the metallic aluminium, can be potentially recovered from the ash and recycled as secondary aluminium. Despite the modest amount of aluminium in the fine fraction, improving metal recovery from such a fraction, by including a grinding stage and advanced ECS in the plant layout, is economical advantageous. In fact, aluminium recovery yield can increase by about 200% with a corresponding direct enhancement of revenues of about 2 Euros per ton of treated bottom ash.

Based on the recovery efficiency previously reported, a forecasting model was developed for evaluating the amount of aluminium scraps potentially recoverable. The model, applied for estimating the situation expected for Italy in the years 2015 and 2020, results in prospected recoveries of about 16,300-24,900 tonnes of aluminium in 2015, with an increase to 19,300-34,600 tonnes in 2020. This corresponds to an amount of secondary aluminium potentially producible included between 11,300-17,300 tonnes in 2015 and 13,400-24,000 tonnes in 2020. Considering that the bottom ash treatment plants currently installed in Italy have a capacity less than half of what will be needed in the future, a good opportunity of development is present in our Country.

Extended applications of recovery options should, thus, be considered as a viable opportunity for enhancing materials recycling from waste to energy in our Country, with positive contributions in the improvement of sustainability related issues in the waste management sector.

SOMMARIO

Il recupero dell'alluminio e dei rottami non-ferrosi dalle scorie di incenerimento dei rifiuti è diventata una pratica diffusa negli ultimi anni. La concentrazione di tali metalli nelle scorie può, infatti, essere superiore a quella in natura, rendendone economicamente vantaggioso il recupero. Bisogna, inoltre, pensare ai benefici ambientali associati al riciclo di questi metalli e ai vantaggi tecnici della loro separazione in vista del successivo recupero della frazione inerte delle scorie.

Sebbene il recupero dei metalli dalle scorie sia una pratica diffusa, la corretta configurazione dell'impianto di trattamento è piuttosto complessa. Molte informazioni sono infatti necessarie, quali l'effettiva quantità di alluminio nelle scorie e le sue principali caratteristiche, in termini di classificazione granulometrica e qualità. In particolare è necessario conoscere il livello di ossidazione dei rottami recuperabili e la presenza di altri metalli non-ferrosi oltre all'alluminio.

Il lavoro svolto nell'ambito del progetto di ricerca ha indagato tre aspetti fondamentali del recupero dell'alluminio dalle scorie di incenerimento di rifiuti:

- Il comportamento dell'alluminio nei forni degli impianti di incenerimento di rifiuti urbani. E' stato valutato il bilancio di massa dell'alluminio, col fine di definire la quantità di alluminio presente nelle scorie in forma metallica e perciò recuperabile e riciclabile;
- Il recupero dell'alluminio dalla frazione fine delle scorie (< 5 mm);
- I quantitativi di alluminio potenzialmente recuperabili dalla scorie italiane in un arco temporale di 10-20 anni.

La valutazione del bilancio di materia dell’alluminio nei forni degli impianti di incenerimento e della sua ripartizione fra i residui della combustione risulta essenziale per definire i quantitativi di alluminio recuperabili dalle scorie. Infatti, le tecnologie correnti sono in grado di recuperare solamente i noduli di alluminio di dimensione superiore al mm. Oltre a ciò, durante la combustione, i rotami in alluminio presenti nel rifiuto subiscono processi di ossidazione e volatilizzazione che ne riducono la massa recuperabile dalle scorie e riciclabile. La conoscenza del livello di ossidazione dell’alluminio nei residui della combustione è, perciò, un’informazione fondamentale per il corretto dimensionamento di un impianto di trattamento delle scorie.

L’entità dei processi di frammentazione e ossidazione è strettamente legata alla struttura e alle proprietà meccaniche dei materiali. Le analisi sperimentali effettuate nel corso del progetto di ricerca su due impianti di incenerimento italiani hanno mostrato che la quantità di alluminio recuperabile dalle scorie aumentata all’aumentare dello spessore dell’imballaggio, come mostrato in Figura A. Circa l’81% dell’alluminio nelle lattine può essere recuperato dalle scorie e successivamente riciclato come alluminio secondario, ma questa quantità si riduce al 51% per le vaschette, al 27% per un mix di imballaggi sottili (foglio in alluminio e foglio poli-accoppiato) e al 47% per il foglio poli-accoppiato con carta. I fogli e le vaschette, di spessore rispettivamente pari a 10-42 μm e 50 μm, sono caratterizzati da una minore efficienza di recupero rispetto alle lattine, il cui spessore è pari a 90-250 μm. Ciò è dovuto alla loro maggiore frammentazione sulla griglia di combustione e alla formazione di noduli più piccoli che si concentrano nella frazione più fine delle scorie. Questi valori suggeriscono, inoltre, che la carta usata nei fogli poli-accoppiati incrementa la resistenza meccanica del foglio in alluminio.

Nel rifiuto indifferenziato, l'alluminio può essere presente sia come imballaggio che sottoforma di altri oggetti, come caffettiere e pentole. La quantità di alluminio recuperabile dalle scorie è, perciò, influenzata dalla composizione del rifiuto e, quindi, dall'efficienza della raccolta differenziata. Considerando la tipica composizione del rifiuto indifferenziato nel nord Italia, circa il 26-37% dell'alluminio alimentato ai forni degli impianti di incenerimento può essere estratto dalle scorie. Ciò corrisponde a una quantità di alluminio secondario producibile pari a circa il 21-23% dell'alluminio alimentato al forno, come illustrato in Figura A. Questi valori si riferiscono ad una situazione dove, a fronte di un'efficiente raccolta differenziata dei rifiuti urbani, la maggior parte dell'alluminio è presente nel rifiuto indifferenziato come imballaggio sottile e quindi si concentra nella frazione fine delle scorie (< 1 mm). Quando la raccolta differenziata è meno efficiente, come in altre regioni italiane, la quantità di alluminio nel rifiuto può essere maggiore e anche le caratteristiche possono essere diverse, con una prevalente presenza degli imballaggi rigidi. In una tale situazione, i quantitativi di alluminio recuperabili dalle scorie potrebbero essere superiori.

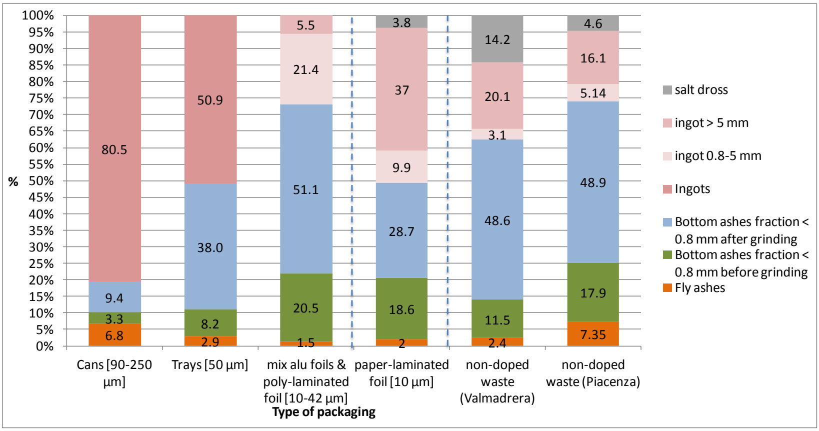

Figure A. Ripartizione dell'Al totale nei residui del processo di incenerimento per 4 differenti tipologie di imballaggio in alluminio e per il mix di alluminio presente nel rifiuto urbano residuo (rifiuto non drogato).

Il recupero dell'alluminio dalle scorie diventa particolarmente complesso quando i noduli hanno dimensione inferiore ai 5 mm. Infatti, le tecnologie tradizionali a correnti indotte, comunemente installate negli impianti di trattamento delle scorie, hanno buone efficienze di recupero solo per i noduli di dimensione superiore a 4-5 mm. L'analisi delle scorie di incenerimento di dimensione inferiore a 4 mm, campionate in un impianto di trattamento svedese, ha mostrato che solamente il 3% dell'alluminio totale presente nella scoria, equivalente al 21% dell'alluminio metallico, può essere recuperato dalle scorie e riciclato come alluminio secondario. Nonostante i modesti quantitativi in gioco, incrementare il recupero dell'alluminio dalla frazione fine delle scorie, con l'introduzione di stadi di triturazione e di tecnologie a correnti indotte più avanzate, è economicamente vantaggioso. Il tasso di recupero dell'alluminio aumenta, infatti, di circa il 200%, con un guadagno netto di circa 2 euro per tonnellata di scoria trattata.

Basandosi sui tassi di recupero prima riportati, è stato sviluppato un modello previsionale per valutare i quantitativi di alluminio potenzialmente recuperabili dalle scorie in Italia al 2015 e al 2020. I risultati mostrano che circa 16,300-24,900 tonnellate di alluminio potranno essere recuperate nel 2015 e questa quantità potrà aumentare a 19,300-34,600 tonnellate nel 2020. Ciò corrisponde ad un quantitativo di alluminio secondario potenzialmente producibile incluso tra 11,300 e 17,300 tonnellate nel 2015 e 13,400-24,000 tonnellate nel 2020. La capacità di trattamento delle scorie attualmente presente sul nostro territorio risulta, però, essere meno della metà di quella necessaria in futuro per poter trattare tutte le scorie di incenerimento prodotte. Il trattamento delle scorie appare, dunque, un settore con un'elevata possibilità di sviluppo.

Estendere le opzioni di trattamento e recupero a tutte le scorie di incenerimento prodotte nel nostro paese può, dunque, essere considerata come un'ottima opportunità per incrementare il recupero e il riciclaggio di materiali nell'ambito del trattamento energetico dei rifiuti, con ripercussioni positive sulla sostenibilità del settore rifiuti.

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1.INTRODUCTION

1.1. SCOPE OF THE WORK

About 4,600,000 tonnes of municipal waste have been incinerated in Italy in 2009, with the production of about 1,200,000 tonnes of bottom ash (ISPRA, 2011). The growing cost of landfilling and the need for reducing the exploitation of natural resources have promoted in the last few years in Europe a fervent research activity on bottom ash treatments aimed at the recovery of metals and at the reuse of the inert fraction, essentially in the cement and concrete industry, as well as in road construction.

These considered treatments are physical, chemical or thermal ones, such as:

- Physical separation of the fine (more polluted) fraction with screens or drums;
- Extraction of metals through magnetic and eddy current separators;
- Washing with water or chemical solvents to remove soluble heavy metals and salts;
- Ageing process to promote the transformation of bottom ash constituents into more thermodynamically stable forms;
- Addition of Al (III) or Fe (III) salts and cements or other bonding agents to reduce the metal mobility through leaching;
- Vitrification or sintering to immobilize heavy metals

into an amorphous glassy phase.

Whatever treatment is used, the recovery of ferrous and non-ferrous metals is an essential step, for both the environmental advantage of metal scraps recycling and the reduction of the negative effects that metals have in some applications including road construction and concrete production (Pecqueur et al., 2001; Muller et al., 2006). Furthermore, the sale of metal scraps represents a significant source of income for bottom ash treatment plants.

However, metals recovery from the bottom ash, and especially the recovery of the non-ferrous fraction, is not an easy task. Achieving a good efficiency of metals separation from the ash needs a proper design of the bottom ash treatment plant, that can become expensive when designed for the recovery of the scraps < 4-5 mm.

A first question can thus rise:

- *Considering that the separated collection is well established in Italy and in the EU Countries, and it will further improve in the future, will be the amount of aluminium that ends up in the residual waste and is routed to incineration sufficient to justify such an investment in the next 10-20 years?*

The answer to this question is *yes*. The problem was tackled in the research project for what concerns the Italian situation, by developing a forecasting model aimed at evaluating the amount of aluminium scraps potentially recoverable in Italy in the years 2015 and 2020. The results show that about 16,300-24,900 tonnes of aluminium might be recovered in Italy in 2015 and this amount will increase at 19,300-34,600 tonnes in 2020. Considering that the bottom ash treatment plants currently installed in Italy have a capacity less than a half of what will be needed in the future, a good opportunity of development is present in our Country.

However the problems of metals recovery is much more complex. Among the number of aspects that need to be analysed, two are the main issues about aluminium recovery from the bottom ash:

- *How much aluminium is present in the bottom ash in its metallic form, i.e. in its recoverable form?*
- *How is it possible to improve aluminium recovery from the fine fraction (< 5 mm) of the bottom ash?*

The aim of the research project was to answer the above two questions.

During the combustion process, the scraps contained in the waste undergo degradation and oxidation processes that determine a loss of their recoverable mass from bottom ash. The thinner fraction might volatilise in the furnace, then leave the waste entrained by the flue gas and subsequently concentrate on the surface of fly ash, both as metallic aluminium and aluminium oxide (alumina – Al_2O_3). The remaining fraction of aluminium, despite remaining in the waste, will certainly undergo surface oxidation: a thin scale of more or less protective oxide is formed on the surface of these scraps, as a consequence of the reactions with oxidizing compounds contained in the combustion flue gas, such as O_2, SO_2, HCl, and molten salts which collect over the metal surface. In this last case, even if we do not measure a reduction of the scrap mass, its recycling potential is lowered because the oxide cannot be recovered in the melting furnace. Such oxidation can be further enhanced when bottom ash is quenched in water after its discharge from the grate (which is the case for the majority of waste incineration plants currently operating in Europe). In fact, the strong thermal shock can break down the oxidation layer, facilitating a further degradation of the scraps. The result of all the processes previously described is a loss of the potentially recoverable aluminium mass, compared to what is fed to the process with the municipal waste.

The actual oxidation level and partitioning of the metal scraps in the incineration furnaces are not yet well known. According to the CEN standard on energy recovery (EN 13431:2004), thin gauge aluminium foil (up to 50 µm thick) shall be considered recoverable in the form of energy, meaning that it is subjected to full oxidation. However, detailed quantitative experimental estimates are not available. Some data about the oxidation levels of flexible and rigid aluminium packaging are reported by Pruvost (2009), but they refer to experiments carried out in 1993 and described in a confidential report. Also Hu et al. (2011) reported the oxidation level of aluminium scraps after their incineration and the influence of combustion conditions on metallic aluminium losses during the incineration process, but they refer to laboratory tests.

During the research project, the behaviour of aluminium in the incineration furnace was investigated to evaluate its partitioning, both as total Al and metallic Al, in the residues of the combustion process and to assess the amount of aluminium potentially recoverable from the bottom ash. The study was carried out on two Italian incineration plants that treat residual waste. Besides investigating the behaviour of the mixed Al in the residual waste (baseline situation), five different aluminium packaging materials were also studied: beverage cans, trays, spray cans, aluminium foil and aluminium poly-laminated foil. The choice of studying aluminium packaging behaviour was based on two considerations: aluminium packaging items are the principal component of aluminium in the waste; in addition their fate in the furnace has important implications for the management of this material, in term of material and energy recovery.

A non negligible amount of aluminium can be found in the bottom ash fraction below 5 mm. The recovery of such fine fraction is possible only when advanced treatment technologies are applied to the bottom ash, including sieving and grinding stages. In fact, standard eddy current separators (ECS) show an average recovery rate of 30%, which drops from almost 100% for particles larger than 20 mm to virtually zero for particle size between 5 and 12 mm, depending on the number of screening steps and on the plant layout and complexity (Berkhout et al., 2011). On the contrary, advanced systems such as wet ECS, magnetic separator and backward operating ECS (Zhang et al., 1999; Settimo et al., 2004; Fraunholcz et al., 2002), included within advanced bottom ash treatment plants comprising several stages of sieving and crushing, might allow to reach higher recovery rates. Muchova and Rem (2007) and Manders (2008) report that some advanced technologies can allow Al recovery rates up to 70%.
This aspect was investigated in the research project by evaluating the amount of Al recoverable from the bottom ash fraction < 4 mm. The investigation was carried out in Sweden, at the Department of Water Resources Engineering of Lund University, and due to the difficulty of recovering the small particles, the alternative to recover H_2 from the bottom ash was also investigated. In fact, metallic Al in the bottom ash can react with water releasing H_2 gas. In normal conditions, during bottom ash storage, H_2 production can pose a safety problem (Mizutani et al., 1999). On the contrary, when the reaction is

promoted in a controlled environment, the recovered H_2 represents a resource, since it can be used as a clean fuel.

1.2. CONTENT OF THE THESIS

The thesis is divided in 6 chapters:

- Chapter 1 briefly defines the topic and the aim of the research project;
- Chapter 2 gives a short introduction to bottom ash treatments for metals recovery, including some information on the oxidation processes that the aluminium scraps undergo in the furnace;
- Chapter 3 deals with the Italian situation about aluminium recovery from the bottom ash, explaining the forecasting model used to estimate the amount of aluminium potentially recoverable from the ash in the years 2015 and 2020;
- Chapter 4 reports the results of the experimental tests carried out on selected aluminium packaging materials to investigate their behaviour in the furnace of waste-to-energy plants;
- Chapter 5 investigates the recovery of aluminium from the fine fraction of the bottom ash (< 4 mm);
- Chapter 6 shows the overall outcome of the thesis and gives suggestions and recommendations for further research.

The research presented in this thesis is partially summarised in 5 papers:

- Grosso, M., Biganzoli, L., Rigamonti, L. (2011). A quantitative estimate of potential aluminium recovery from incineration bottom ashes. Resources, conservation and recycling 55, 1178-1184

- Biganzoli, L., Gorla, L., Nessi. S., Grosso, M. (2012). Volatilisation and oxidation of aluminium scraps fed into incineration furnaces. Waste Management 32, 2266-2272
- Biganzoli, L., Ilyas, A., van Praagh, M., Persson, K., Grosso, M. (2013). Aluminium recovery vs. hydrogen production as resource recovery options for fine MSWI bottom ash fraction. Waste Management. DOI: 10.1016/j.wasman.2013.01.037
- Biganzoli, L., Grosso, M., Forte, F. (2013). Aluminium mass balance in waste incineration and recovery potential from the bottom ash: a case study. Waste and Biomass Valorization. DOI: 10.1007/s12649-013-9208-0
- Biganzoli, L., Grosso, M. (2012). Aluminium recovery from waste incineration bottom ash and its oxidation level. Waste Management and Research (submitted)

In addition, the following publications were produced during the PhD study:

- Biganzoli, L., Grosso, M., Giuliano, M., Campolunghi, M. (2012). Chemical and sewage sludge co-incineration in a full-scale MSW incinerator: toxic trace element mass balance. Waste Management and Research 30, 1081-1088
- Grosso, M., Biganzoli, L., Rigamonti, L., Cernuschi, S., Giugliano, M., Poluzzi, V., Biancolini, V. (2012). Experimental evaluation of PCDD/Fs and PCBs release and mass balance of a WTE plant. Chemosphere 86, 293-299

2. INTRODUCTION TO METALS RECOVERY FROM BOTTOM ASH

2.1. BOTTOM ASH TREATMENTS

Bottom ash is the main residue, in quantitative terms, of MSW incineration. Its production depends on the inert content of incinerated waste and on the type of furnace technology and bottom ash extraction system. For grate furnaces, two bottom ash extraction systems can be applied: wet and dry. In the wet system, bottom ash is quenched in a water bath after its discharge from the furnace. This is the most popular technology, used in most of the European incineration plants. However it has the disadvantage of increasing the moisture of the bottom ash and thus its mass. The average production of bottom ash is, in fact, 15-25% in mass of the incinerated waste for the wet extraction system and 12-20% for the dry one.

The composition of the bottom ash is similar to that of the gravel, especially of the igneous rocks like granites and basalts, with the silicates and the alumina-silicates of Ca, Mg and Fe which are the main constituents, as reported in Table 2.1. Usually silicates and oxides constitute the coarse fraction whereas sulphates, carbonates and most of the heavy metals are the main components of the fine fraction (Marchese et al., 2005). Moreover, bottom ash has a pozzolanic behaviour, typical of the amorphous or partially crystalline materials. All these factors make it suitable in principle to be used as a construction material.

However, compared to natural gravel, bottom ash has a more heterogeneous size distribution and, above all, it has a higher concentration of metals, as reported in Table 2.2. This requires some treatments to increase its mechanical properties, in view of the recovery of the inert material, as well as to improve its environmental properties, preventing the negative environmental impacts that a direct reuse of the raw bottom ash can cause due to its high content of heavy metals and polluting agents.

These treatments include physical, chemical or thermal processes.

Table 2.1. Principal mineral compounds in bottom ash. Value are expressed as % of the bottom ash mass (ADEME, 2008).

Al_2O_3	**CaO**	**Fe_2O_3**	**K_2O**	**MgO**	**MnO**	**N_2O**	**P_2O_5**	**SiO_2**
8.66± 6.25	17.68± 15.37	8.68± 2.84	1.08± 0.78	2.52± 2.10	0.12± 0.08	4.73± 2.84	1.26± 0.88	48.40± 41.13

Table 2.2. Concentration of heavy metals in bottom ash according to the literature (Biganzoli, 2008).

Metal	**As**	**Cd**	**Cr**	**Hg**	**Ni**	**Pb**	**Sb**	**Zn**
(μg g^{-1})	1.4-114	0.25-11	0.5-1800	0.06-0.9	28-800	194-5000	10-147.5	300-8890

Physical separation

Physical separation includes size classification and separation of specific materials, like metals, from the bulk stream of the bottom ash.

Size classification is a fundamental step in a bottom ash treatment plant and allows to isolate the more contaminated fine fractions, upgrading the quality of the residual stream. In addition, this treatment is preparatory for metals separation, improving the efficiency of the ferrous and non-ferrous scraps recovery.

Size classification can be performed through both dry and wet processes. Dry separation operates with standard drums or flat deck screens with a typical mesh size of 20-50 mm and 2-10 mm. Wet separation can be performed through dense medium separation or attrition washing. Compared to dry separation, the presence of water allows the extraction of soluble constituents, improving the bottom ash quality, but it generates more fine material to be disposed off and requires the subsequent water treatment (Polettini et al., 2007).

Ferrous and non-ferrous scraps can be separated from the bottom ash by using magnets and eddy-current separators. Their recovery is an essential step of the bottom ash treatment process, both for the environmental advantage of metal scraps recycling and for the reduction of the negative effects of metals like Al, Fe and Zn which can result in swelling and expansion in some applications like road construction and concrete production (Baun et al., 2007; Polettini et al., 2007).

Ferrous and non ferrous metals are present in the bottom ash in a range of 7-15% and 1-2%, respectively (Sabbas et al., 2003; Baun et al., 2007). Non ferrous metals consist of aluminium, for more than 60%, and copper, brass and precious metals, such as gold, in minor quantity.

The recovery rates of ferrous and non ferrous metals from the bottom ash is equal to about 60-80% and 25-35% of their amount in the waste, respectively. More detailed information about non-ferrous metals recovery is reported in Chapter 2.2.

Chemical separation

After the physical separation, bottom ash can be treated to remove salts and heavy metals.

Washing with water is a common and simple treatment to be performed after a dry size classification. This treatment allows to remove the soluble components like chloride, sodium and sulphate. The removal efficiency of sulphate is, however, usually insufficient to comply with the leaching level required by the regulation. To improve sulphate solubilisation, $NaHCO_3$ or CO_2 can be used in the washing solution, improving the precipitation of Ca as carbonate in place of sulphate forms (Polettini et al., 2007).

For what concerns heavy metals, the efficiency of the process is usually low, since fresh bottom ash is an alkaline material and the pH of the resulting fresh bottom ash/water suspension is typically included between 9.5 and 12, corresponding to the range of minimum solubility for most metal species. A certain metal extraction capability may be observed towards Cu and to some extent Cr and Pb, but always inadequate to reduce leaching below regulatory limits. To improve metals leaching, CO_2 can be added during water washing, with positive effects on Cu, Ni and Zn (Polettini et al., 2007; Ragaglia, 2004; Polettini et al., 2005).

Chemical extraction can reach a better performance when inorganic acids (like hydrochloric, nitric or sulphuric acid), chelating agents (like nitrilotriacetate (NTA), ethylendiamine-tetraacetate (EDTA), diethylentriaminepentaacetate (DTPA)), and saponins are used in substitution of the water. The extraction process usually involves one to three extraction steps, followed by one to three distilled water washing steps to remove the excess of the chemical agents used for the treatment.

Chemical stabilisation

The aim of these treatments is to promote the formation of low-solubility minerals, thermodynamically and geochemically stable.

A first stabilisation can be performed through the natural weathering: bottom ash is stockpiled under atmospheric conditions for 3-12 months, eventually irrigated with water. Reactions of hydrolysis, dissolution/precipitation, neutralisation, redox, carbonation, surface complexation, surface precipitation, adsorption[1] take place when the ash comes in contact with the atmospheric agents (water, oxygen and CO_2) and promote the mineralogical transformation of the ash and the decrease of pH from 11-12 to 8-10. This modifies the leaching-controlling mechanisms, altering the release of the principal ions and trace elements from bottom ash, thus reducing the leaching phenomena during the ash recovery or disposal. The main alterations of the composition and of the leaching and geotechnical properties take place within five months, when the pH decreases, the organic matter is degraded, the chlorates are washed and the carbonates precipitate.

The acceleration of the process can be achieved by flushing the bottom ash with a gas stream enriched in CO_2. This process is called accelerated carbonation. It can be performed under dry

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[1] The main weathering reactions are:

- Carbonation: CO_2 (gas) + $Ca(OH)_2 \rightarrow CaCO_3 + H_2O$ (Eq. 2.1)

- Sulphate destabilization: $CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$ (Eq. 2.2)

  $CaSO_4*H_2O \rightarrow Ca^{2+} + SO_4^{2-} + H_2O$ (Eq. 2.3)
- Formation of hydrocalcite ($Ca_2Al(OH)_6[Clx(OH)x]*3H_2O$) (Eq. 2.4)
- Formation of ettringite ($Ca_6A_l(SO_4)_{3(}OH)_{12}*26H_2O$) (Eq. 2.5)

conditions, injecting the CO_2 flux through the bottom ash stockpiles, or wet conditions, working on a slurry solution of bottom ash and water. In the first case, the time needed to stabilise the ash is in the order of about one month and the modifications of the physical and chemical characteristics of the ash are similar to those of the natural weathering. The time is further shortened when the ash is mixed with water. However, in this case, the results can significantly change according to the applied L/S ratio. When a high L/S ratio (5-20 on weight) is used, the treatment is more similar to a chemical washing of the ash, promoting the release of the metals, than to a weathering process (Rendek et al., 2006; Fernandez-Bertos et al., 2004; Costa et al., 2007).

A true chemical stabilisation can be achieved with the addition of species capable of increasing the sorption properties of the material, with positive effects of metals immobilisation. Al(III) and Fe(III) salts promote Cu and Cr and Sb oxides immobilisation through the precipitation of Al and Fe (hydr)oxides, but they do not have any effect on Ni, Zn, Ca, Na and Mn (Comans et al., 2000; Polettini et al., 2005). Soluble phosphates induce the surface sorption of metals onto phosphate phases and their precipitation as apatites (Crannel et al., 2000; Ragaglia, 2004).

Blending with cement or other binders is also a process that can be applied to the bottom ash, in order to reduce the leaching of heavy metals. Bottom ash has in fact a pozzolanic behaviour, making it suitable to be used in concrete production or as a construction material.

Thermal treatments

The principal thermal treatments applied to the bottom ash are sintering and vitrification. Their aim is to reduce the volume of the residues and to improve their characteristics in term of mechanical strength, porosity, water adsorption, chemical stability and leaching of contaminants (Polettini et al., 2007).

Vitrification is performed at 1000-1500°C; the bottom ash is melted and a homogenous liquid phase is generated, which is rapidly cooled producing an amorphous glassy phase. Sintering is conducted at a temperature of about 900°C, below the melting point of the main bottom ash constituents. The contaminants are bounded into a low porosity and high resistance solid phase. In both treatments, a particular attention must be reserved to the high volatile metals (Hg, As, Cd, Zn) and some organic compounds like the PAH, which can volatilise at temperatures from 800°C to 1300°C (Kuo et al., 2003).

The high energy consumption and thus the high costs have limited the applicability of these technologies in Europe. However, the vitrification and the sintering of the bottom ash can be achieved contextually to the waste treatment in other waste-to-energy technologies than incineration, like in gasification and in pyrolysis, reducing the overall costs of waste and bottom ash treatment.

2.2. NON–FERROUS METALS RECOVERY

The treatments applied to the bottom ash to make its reuse possible and safe from an environmental point of view include in all cases the removal of the metal scraps. While ferrous metals separation has a longer tradition, in recent years the recovery of the non-ferrous fraction has also become a quite common practice (Astrup et al., 2007), fostered by the avoided problems of swelling and expansion that metals, especially aluminium, cause when bottom ash is reused in concrete production or in road construction (Pecqueur et al., 2001;

Muller and Rubner, 2006) and by the environmental advantages connected to its recycling, as illustrated in Figure 2.1. The benefits in terms of CO_{2eq} emission saving associated to the treatment and the recovery of the bottom ash was evaluated through Life Cycle Assessment methodology (Grosso et al., 2010). Despite the amount of aluminium scraps in the bottom ash is about 6 times lower than that of the ferrous scraps, the saving of CO_{2eq} connected to their recovery and recycling is absolutely comparable.

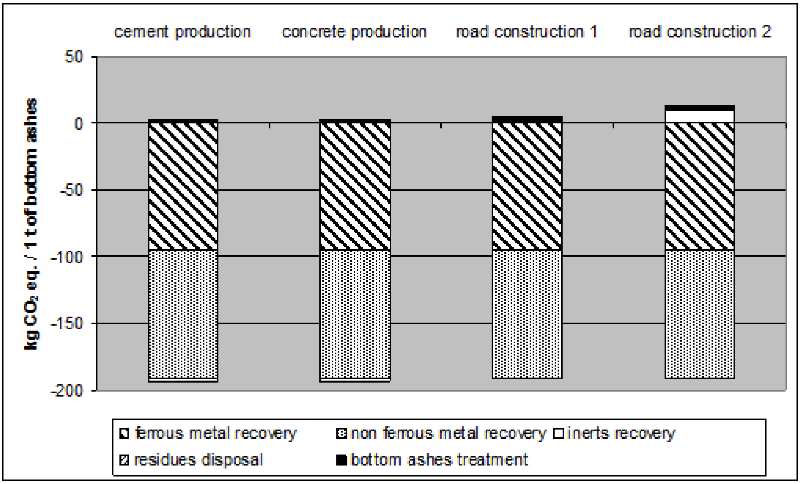


Figure 2.1. Contribution of each sub-process of the bottom ash treatment process to the Global Warming Indicator (GWP_{100}) for the treatment of 1 tonne of bottom ash (Grosso et al., 2010).

Non-ferrous metals are removed from the flow of inert material through Eddy Current Separators (ECS). The working principle of an ECS is quite simple: an electrical charge is induced into a conductor by changes in the magnetic flux cutting through it. Such changes in the magnetic flux can be achieved by moving permanent magnets past a conductor. The effect of these currents is to induce a secondary magnetic field around the particle; this field reacts with the magnetic field of the rotor, resulting in a combined driving and repelling force that literally ejects the conducting particle from the product stream. In most of the ECS systems, a high speed magnetic rotor is fitted within a non-metallic drum which travels much more slowly than the rotor so as to produce flux variations at the surface of the drum; the drum also acts as the head pulley of the conveyor carrying the product to be separated. When the conducting particles (any metallic objects) are carried by the conveyor over the drum, the magnetic field passing through the particles induces currents into them. Since these particles are of random shapes, it is difficult for the induced current to flow within them in an orderly manner and the currents therefore tend to swirl around within the particles, hence eddy current. Non-ferrous metals, in contact with the magnetic field, are rejected with a force that is proportional to the ratio between their conductivity and their specific weight and pushed away with different trajectories from those of the inert material, whose stream is collected separately.

The ECS machine requires a proper calibration, performed on the basis of the size of the material to be separated. Higher yields are obtained with pieces sizes included between 5 mm and 15 cm, and for material flows below 15 tonnes h^{-1} (Maglio, 2003). For these reasons, the first stage of size classification is essential in order to obtain different material flows of similar size, with a magnetic separator and an ECS sequentially located on each stream.

The recovery efficiencies of non-ferrous scraps from the bottom ash, as reported by different authors, are compiled in Table 2.3. On average, standard ECS show a 30% recovery efficiency with respect to the aluminium fed into the furnace of the WTE plant, which corresponds on average to 1% of the bottom ash mass. However, some advanced technologies such as wet eddy current separators (WECS), Magnus ECS, backward operating ECS (Zhang et al., 1999; Settimo et al., 2004; Fraunholcz et al., 2002), included within advanced bottom ash treatment plants comprising several stages of sieving and crushing, can reach higher recovery rates by improving the selective separation of small non-ferrous metal particles below 2-5 mm (De Vries et al., 2009).

The working principle of these devices is here briefly described. Backward operating ECS is a standard separator whose magnetic drum rotated in the "backward" or counterclockwise manner. Zhang et al. (1999) showed that, if it is difficult to separate small metal particles from the non-metal stream when the magnetic drum rotates in the "forward" mode, the yield improves drastically when it rotates in the opposite direction. The Magnus ECS working is based on the "Magnus effect": a spinning particle moving through a fluid experiences a force perpendicular both to its direction of motion and to the axis of rotation, as illustrated in Figure 2.2 (Fraunholcz et al., 2002). This effect can be used to recover small non-ferrous metal particles from the bulk stream (both wet and dry). The Magnus separation process consists of passing a feed stream to a fast-spinning magnet in order to create a selective rotation of the non-ferrous particles so as to deflect away from the stream by the Magnus effect. Since this force derives from the fluid around the particles, it is not necessary to feed the material in a monolayer (Settimo et al., 2004). In a wet ECS, the water allows to glue all the particles to the belt surface. For small particles, this adhesive force is of the same order of magnitude as gravity. Without the action of the rotor, therefore, virtually all particles would stick to the belt and end up in the non-metal fraction. However, the rotating magnetic field makes the metal particles (both the ferrous and the non ferrous particles) spin, with the effect that the water bonds between these particles and the belt are broken. If the magnetic attraction on the ferrous particles is sufficiently large, these will remain in the surface of the belt, but the non-ferrous metal particles will be liberated at some point and follow more or less the same path of a traditional ECS, as illustrated in Figure 2.3. On the contrary, the adhesive force is strong enough to keep most of the non-metal particles glued to the belt surface. Since the force necessary to break the adhesive forces is small, poorly conductive and heavy non-ferrous particles are also recovered (Settimo et al., 2004).

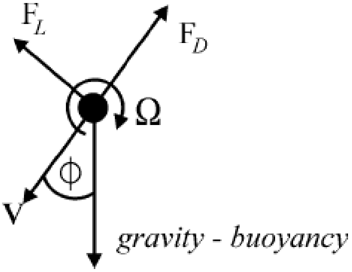


Figure 2.2. Force diagram for a particle that rotated at an angular velocity Ω while settling with a linear velocity V with respect to a fluid. F_L is the lift force and F_D is the drag force (Fraunholcz et al., 2002).

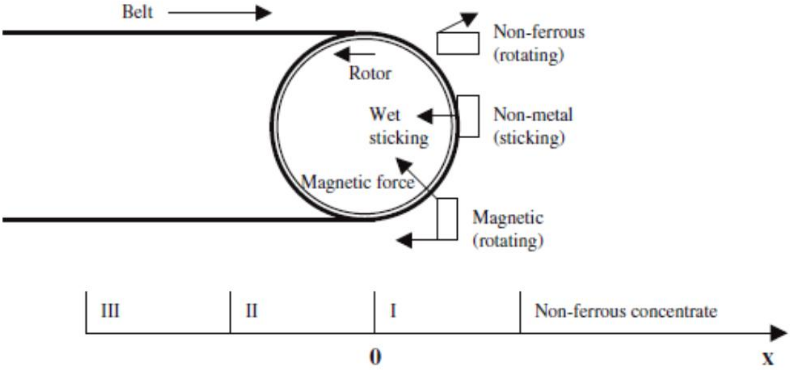


Figure 2.3. Wet magnetic separation with a counter-rotating magnet rotor. Non-metals end up in compartments I, II and III; ferrous metals in compartments I and II (Settimo et al., 2004).

From an economical point of view, the higher investment required for advanced bottom ash treatment plants, primarily due to the introduction of a grinding stage and the presence of one eddy current for each size stream, is justified by the increase of aluminium recovery, as reported by Kohaupt (2011). For small incineration plants, which cannot afford such an investment, a good option might be the collaboration with a centralised bottom ash treatment plant, which serves several incineration plants, or with mobile treatment plants.

However, the recovery efficiency of aluminium scraps does not only depend on the ECS technologies or the bottom ash treatment layout. It is strictly related to the type of aluminium material that is present in the waste, if it is mainly present as packaging or not and which type of packaging item. Where the aluminium source separation level implemented in the upstream management system is modest, the unsorted waste can contain a significant amount of rigid aluminium packaging items (like cans and spray cans), whose recovery from the bottom ash is quite easy, as illustrated in Chapter 4 of this thesis. On the contrary, where an effective separated collection is implemented also for the metals, most of the aluminium in the unsorted waste is present as flexible packaging (foil and poly-laminated foil), whose recovery is complex with standard technologies. Data reported in Table 2.3 should, thus, be interpreted according to the waste collection system implemented in the country of analysis at the time of the paper publication. In addition, the procedure used for the evaluation of the ECS efficiency is not always clearly explained and sometimes these values refer to the total of non-ferrous metals, without considering the sole aluminium fraction and its pureness. This makes quite complex the correct interpretation of the data in Table 2.3 and their comparison.

Table 2.3. Recovery rate of aluminium from MSW incineration bottom ash.

References		u.o.m.	recovery rate
Magnus Project NL, 2003		% in mass (recovered Al /bottom ash)	1.77
Aluminium and Miljo, DK, 2003	Kara > 6 mm	% in mass (recovered Al /bottom ash)	0.36
	Vestforb. > 6mm	% in mass (recovered Al /bottom ash)	0.128
	Vejen > 6 mm	% in mass (recovered Al /bottom ash)	0.288
	Odense > 6 mm	% in mass (recovered Al /bottom ash)	0.352
Rem et al., 2004	impianto AEB pilota	% in mass (recovered Al /bottom ash)	1.2
Association of incinerators NL, 2006		% in mass (recovered Al /bottom ash)	0.7-1.5
CiAl, 2006		% in mass (recovered Al /bottom ash)	0.49-1.17
Alu DK, 2006		% in mass (recovered Al /bottom ash)	0.65-0.78
Muchova et al., 2006	Pilot plant AEB	% in mass (recovered Al /bottom ash)	1.62
Muchova and Rem, 2007		% in mass (recovered Al /bottom ash)	0.35-1.05
Astrup et al., 2007		% in mass (recovered Al /bottom ash)	0.16-0.4
Barcellesi, 2008		% in mass (recovered Al /bottom ash)	0.8
Lamers, 2008		% in mass (recovered Al /bottom ash)	0.8
		% in mass (recovered Al /Al in the bottom ash)	32
France aluminium recyclage, 2006		% in mass (recovered Al /Al fed into the furnace)	35
Association of incinerators NL, 2006		% in mass (recovered Al /Al fed into the furnace)	48.2
Muchova and Rem, 2007	State of the art	% in mass (recovered Al /Al fed into the furnace)	9-28
	Pilot plant AEB	% in mass (recovered Al /Al fed into the furnace)	80

Table 2.3. (follow) Recovery rate of aluminium from MSW incineration bottom ash.

References		**u.o.m.**	**recovery rate**
Muchova and Rem, 2007	State of the art in NL 0-2 mm	% in mass (recovered Al /Al fed into the furnace)	0
	State of the art in NL 2-6 mm	% in mass (recovered Al /Al fed into the furnace)	7
	State of the art in NL 6-20 mm	% in mass (recovered Al /Al fed into the furnace)	45
	State of the art in NL >20 mm	% in mass (recovered Al /Al fed into the furnace)	86
	Pilot plant AEB 0-2 mm	% in mass (recovered Al /Al fed into the furnace)	0
	Pilot plant AEB 2-6 mm	% in mass (recovered Al /Al fed into the furnace)	83
	Pilot plant AEB 6-20mm	% in mass (recovered Al /Al fed into the furnace)	87
	Pilot plant AEB >20 mm	% in mass (recovered Al /Al fed into the furnace)	n.d.
Manders, 2008	multistep unit	% in mass (recovered Al /Al fed into the furnace)	55-65
	Advance design	% in mass (recovered Al /Al fed into the furnace)	70
Pruvost, 2009	State of the art in France	% in mass (recovered Al /Al input to the bottom ash treatment plant)	65-70

2.3. ALUMINIUM OXIDATION PROCESS IN THE INCINERATION FURNACE

Even if they are deprived of all the possible impurities, aluminium lumps are always characterized by a oxidized surface, as a result of the thermal oxidation processes that occur inside the furnace. The oxidation level of aluminium lumps is closely connected to their dimensions: the smaller the size, the greater is the specific surface area exposed to oxidation processes. In addition, most incineration plants are equipped with a wet system for the discharge of the bottom ash, meaning that the bottom ash is quenched in a water bath. The contact with water during the quenching of the bottom ash causes the oxide scale to break up very easily because of the strong thermal shock, thus exposing the underlying layer of metallic aluminium to further oxidation and significantly lowering its potential recovery, similarly to what happens to ferrous scraps (Lopez-Delgado et al., 2003). The presence of aluminium oxide in the scraps promotes the formation of foams during the melting process because the oxide is characterized by a lower density than aluminium. As it happens in the production of secondary aluminium, foams are removed but, along with them, part of the molten aluminium is inevitably lost. For this reason, aluminium lumps resulting from bottom ash treatments are fed in small percentages to the saline furnaces for the production of secondary aluminium, excluding the finest material in order to avoid dramatic drops in terms of recovery yields.

The present chapter describes the oxidation processes that involve the aluminium scraps in the incinerator furnaces.

Aluminium corrosion in high-temperature oxidizing atmospheres

Alumina (Al_2O_3) is the only thermodynamically stable solid oxide of aluminium. The oxide can exist in various forms: the most common forms are the γ and the α phases, but also δ-Al_2O_3 has been identified in scales formed at 900°C. The γ is the stable phase at temperatures below 900-950°C and it turns into the α phase when it is heated to high temperatures (above 900-1000°C), at which the α phase, called corundum, is the thermodynamically stable modification. The reverse transformation, however, does not take place on cooling. Although Al_2O_3 is the only stable solid oxide of aluminium, the vapour species at high temperatures comprise Al_2O and AlO.

The α-alumina is characterized by a low concentration of electronic and ionic defects and, as a consequence, the transport of the reactants forming the oxide (metal cations and oxygen anions) through the scale is very slow. Probably this is related to the fact that this oxide has a large band gap (950-1050 kJ/mol) and high lattice energy.

With regard to the oxide scale growth, Al_2O_3 scales have constant ionic conductivity in the pressure range $1\text{-}10^{-15}$ atm of O_2, while electronic conductivity predominates at lower oxygen pressures. This suggests that part of the oxide growth is governed by electron transport. However, the growth of alumina scales is more complicated and the transport of the reactants in all probability takes place along grain boundaries. Inward oxygen transport seems to be the principal mechanism for scale growth, however the wrinkling and convolutions of alumina scales suggest that oxide formation takes place also within the scales and that some outward diffusion of aluminium occurs. Furthermore, it is important to notice that diffusion in poly-crystalline samples is appreciably higher than that in single-crystal specimens.

During the initial stage of oxidation, aluminium develops a transient, metastable scale (γ and δ alumina), which grows more rapidly than α-Al_2O_3. The metastable alumina species have lower density than α-Al_2O_3 and their transformation in α-Al_2O_3 is accompanied by a 13% reduction in volume (Young, 2008).

Thanks to the formation of Al_2O_3 protective scale, aluminium is generally used in alloy with other elements such as chromium and silicon, to reduce the effects of corrosion process. Alumina scales generally provide better oxidation resistance and lower oxidation levels than chromia scales, especially at high temperatures. Instead, for temperatures below 800°C the aluminium-forming alloys are more susceptible to corrosion than the chromia-forming ones. This can be explained by considering that the transient scales forming on alumina-forming alloys contain a larger proportion of spinel phase than chromia-forming alloys and, moreover, that the alumina formed in this range of temperature does not consist of the highly protective α-Al_2O_3, but rather of the less protective γ-Al_2O_3. Alumina does not suffer from oxidative evaporation and alumina-forming alloys can be used at higher temperatures than chromia-forming alloy, from an oxidation point of view. Furthermore, the capacity of alumina to delay sulphidation is better than that of chromia, but the duration of the protective period also depends on the adhesion and mechanical integrity of the scales and the nature of the sulphidizing environment. In presence of molten Na_2SO_4, alumina may dissolve through both acid and basic mechanisms, following the reactions:

$$Al_2O_3 + 3SO_3 = 2Al^{3+} + 3SO_4^{2-} \quad \text{(Eq. 2.6)}$$

$$Al_2O_3 + O^{2-} = 2AlO^{2-} \quad \text{(Eq. 2.7)}$$

However, Al_2O_3 is very stable towards basic fluxing and, moreover, for combustion gases at high temperatures, even those containing up to several percentages of SO_2, the SO_3 level probably never becomes sufficiently high for acid fluxing to constitute an important problem.

Corrosion of aluminium is also affected by the morphology and composition of the item/scrap (Soler et al., 2007). The concentration of alloying elements modifies the oxidation behaviour of the item/scrap. Certain elements strengthen the protective properties of the oxide film by forming mixed oxides, while others, on the contrary, promote aluminium oxidation. Tenorio and Espinosa (2000) compared the oxidation behaviour of two aluminium alloys used for beverage cans. Lid is made up of the alloy AA5182, which is composed for 4-5% of Mg, for 0.2-0.3% of Mn, for 0.2% of Si and for 0.35% of Fe, whereas the body of the can is made up of the alloy AA3004, composed for 0.8-1.3% of Mg, for 1-1.5 % of Mn, for 0.3% of Si and for 0.7% of Fe. Up to temperatures of 700°C, the oxidation kinetic of the lid material is greater than that of the body alloy due to the higher concentration of Mg, which has a greater affinity with oxygen than aluminium. However, for temperatures higher than 750-800°C, the oxidation kinetic of the body changes and becomes linear. This suggests a loss of the initial protective characteristics.

Aluminium corrosion in aqueous solutions

The fundamental reaction of aluminium corrosion in aqueous media (Vargel, 2004) is the following:

$Al + 3H_2O \rightarrow Al(OH)_3 + 3/2H_2$ (Eq. 2.8)

Aluminium corrosion results in the formation of $Al(OH)_3$, which is insoluble in water and precipitates as a white gel, and in the production of hydrogen gas. The corrosion reaction determines the rapid passivation of aluminium, which is recovered with an $Al(OH)_3$ layer (Stockburger et al., 1991).

The corrosion process is more aggressive in the presence of alkaline solutions. High pH values, in fact, can reduce aluminium surface passivation, enhancing aluminium corrosion. For example, in the presence of NaOH the reactions involving aluminium are:

$2Al + 6H_2O + 2NaOH \rightarrow 2NaAl(OH)_4 + 3H_2$ (Eq. 2.9)

$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3$ (Eq. 2.10)

Initially, the hydrogen generation reaction consumes sodium hydroxide, but when the aluminate concentration exceeds the saturation limit, the aluminate undergoes a decomposition reaction that produces a crystalline precipitate of aluminium hydroxide with the regeneration of the alkali. The presence of OH^- ions promotes the dissolution of the oxide layer according to the reaction:

$$Al(OH)_3 + OH^- \leftrightarrow Al(OH)^{-4} \qquad \text{(Eq. 2.11)}$$

and thus facilitates the reaction between exposed Al and water and improves the corrosion rate (Soler et al., 2009).

The production of hydrogen can lead to another mechanism of corrosion, named stress corrosion. This type of corrosion results from the combined action of a mechanical stress and a corrosive environment. The formation of an $Al(OH)_3$ layer on the aluminium surface traps water molecules that continue to react with the metal to produce hydrogen (Ishii et al., 2007), which remains under the passive layer until the pressure of the gas is able to break it. In the presence of cracks, the oxide film does not protect aluminium, so it reacts with water and releases new hydrogen, which concentrates at grain boundaries and promotes intercrystalline dechoesion.

Aluminium scraps corrosion in WTE plants

Aluminium packaging and other aluminium items contained in the waste fed to WTE plants undergo oxidation processes in the furnace (representing a typical high temperature oxidizing environment).

Moreover, the amount of aluminium that is not transported by the flue gas with fly ash concentrates in bottom ash and, when it is quenched in water, can undergo a further corrosion process. The strong thermal shock can lead to the breakdown of the oxide layer, facilitating a further degradation of the scraps. In addition, the high pH values of the quenching water promote the dissolution of the alumina protective scale. At high pH values, a uniform corrosion of aluminium surface takes place because the dissolution rate of the oxide film is greater than its rate of formation. This type of corrosion develops as pits of very small diameter, in the order of a micrometer, and results in a uniform and continuous decrease in thickness over the entire surface area of the metal.

The type of bottom ash discharge method adopted by the WTE plant, wet or dry, therefore can strongly influence the oxidation rate of aluminium scraps recoverable from bottom ash and thus their recycling efficiency. Lopez-Delgado et al. (2003) observed that the oxidation level of ferrous scraps recovered from bottom ash is lower when they are not quenched in water, as in the case of fluidized bed combustion furnaces. This can be extended with a certain probability to non-ferrous scraps.

Laboratory tests carried out by Buekens in 1993 (Pruvost, 2011) show that the oxidation level of aluminium differs from one type of packaging to the other. On average, when the item is exposed to a reducing atmosphere at 500°C for about 30 minutes and then to an oxidizing atmosphere for 30 minutes at 500°C and for other 30 minutes at 1100°C, the oxidation level is included between 2% and 20%. When the item is exposed for one hour at 800°C with shredding every 10 minutes, it is included between 0.5% and 40%, as reported in Table 2.4. Full-scale tests, carried out on an incineration plant equipped with a dry extractor for bottom ash, showed that 84% of the flexible laminates and 60% of rigid packaging can be recovered from the bottom ash with an oxidation level of about 60% and 26% respectively, as illustrated in Table 2.5.

Controlled laboratory pot furnace tests, carried out by Hu et al. (2011) using household waste with different aluminium packaging types (thin foils, foil containers and beverage cans), produced metallic aluminium recovery yields between 77 wt.% and 93 wt.% (Figure 2.4), which varied as a function of the type of packaging. In addition, the type of aluminium packaging affects the resulting size distribution, while the input shape (crumbled or sheet) has only a moderate influence.

Furthermore, the oven tests showed that physical, thermal and chemical factors might promote metallic aluminium losses by enhancing the oxidation processes in the furnace. The main influencing factors were, in decreasing order, the packaging type, combustion temperature, residence time and salt contamination.

Table 2.4. Results of laboratory tests carried out by Buekens (1993) on aluminium packaging (Pruvost, 2011).

Material	**% Al**	**½ h 500°C reducing atmosphere ½ h 500°C and ½ h 1100°C oxidizing atmosphere**		**1h 800°C shredding every 10 min**	
		Oxidation %	**Thickness oxide µm**	**Oxidation %**	**Thickness oxide µm**
Yoghurt lid Al 37 µm	93.9	19.4	10.8	8.2	4.6
Cheese pack Al 37 µm PE/EVA 30µm	77.1	13.3	7.4	0.6	0.3
Blister Al 30µm PE 30 µm	74.6	11.2	5.1	10.6	4.8
Biscuit pack Al 7-9 µm Paper 40 µm	28.4	23.6	2.9	42	5.2
Sachet Al 30µ m LDPE 30 µm Paper 40 µm	54	3.9	1.8	4.4	2
Household foil Al 7-9 µm	100	n.a.	n.a.	7.8	0.9

Table 2.5. Results of full-scale tests carried out by Buekens (1993) on aluminium packaging (Pruvost, 2011).

Residues	**Flexible packaging (Al 7µm-Paper-PE)**		**Rigid packaging (aerosol containers)**	
	Partitioning %	**Oxidation %**	**Partitioning %**	**Oxidation %**
Bottom ash	84	60	61	26
Fines under the grate	10	21	39	2
Fly ash	6	13	0	-

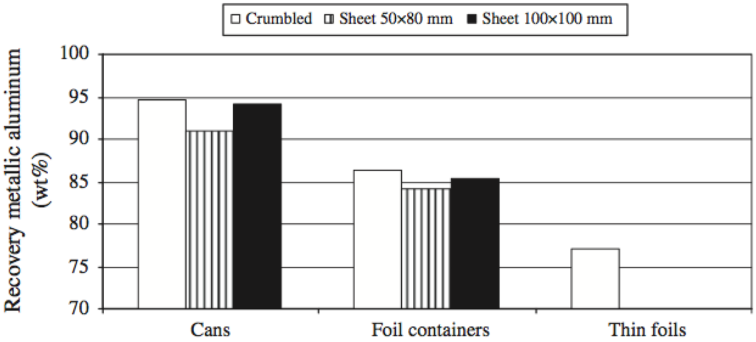


Figure 2.4. Results of laboratory pot furnace tests carried out by Hu et al. (2011) on aluminium packaging.

3. POTENTIAL ALUMINIUM RECOVERY FROM BOTTOM ASH IN ITALY

In 2007 in Italy, only 20% of the produced bottom ash was treated and 421 t of aluminium were recovered. Most of the plants installed in our Country are aimed at recovering the bottom ash inert fraction for concrete production. Some new plants were built in the last years to recover the bottom ash in road construction, but due to problems in their authorisation they are still not operating.

From a legislative point of view, the recovery of bottom ash is regulated by the D.M. n. 186 of the 5th of April 2006 about the recovery of hazardous waste in simplified regime. The law allows to use the bottom ash for clinker production, being understood that the produced clinker must comply with all the environmental and quality characteristics necessary for the "UE label" and defined by the UNI EN 12620:2003, UNI 8520-1: 2005 and UNI 8520-2:2005.

The potential for material recovery from the bottom ash in Italy is thus interesting, due to the lack of plants compared to other European Countries, like the Netherlands, Denmark, France and Germany, where more than 70% of the bottom ash is recovered and reutilised (Crillensen and Skaarup, 2006).

For what concerns the recovery of the metal fraction, even if metal scraps in the residual waste (URW) are expected to decrease according to a framework where overall source separation levels are increasing, as requested for example by the EU Directive on waste (2008/98/EC), the amount of metals potentially recoverable from the bottom ash will probably increase in the next ten years in our Country. Italy has, in fact, an interesting growing potential for waste incineration. Only 12.1% of the waste was incinerated in 2009, with 49 plants operating (ISPRA, 2011). According to the regional waste management plans, the number of plants operating in our Country should increase in the next ten years, with 25 new plants and lines to be installed. These plans seem quite ambitious and it is difficult to believe that all the planned plants will actually be built as for 2020. In any case, even if only a part of the planned plants will be actually operating until 2020, the amount of bottom ash, and hence metals, available for recovery will surely increase.

A quantitative estimate of the aluminium potentially recoverable from the bottom ash and then recyclable as secondary aluminium in Italy in 2015 and 2020 is presented in this chapter. The model used for the evaluation is described in Grosso et al. (2011) and more in details in CiAl (2011), where the historical data from 2000 to 2007 were considered for the evaluation. In this chapter the updated version of the study will be presented, where the input data were updated at 2009 where possible. In addition, the results of the research about aluminium oxidation, presented in Chapter 4, were introduced in the evaluation.

3.1. MODEL DEFINITION

The amount of aluminium scraps which can be recovered and recycled from bottom ash has been evaluated through a model specifically developed for this purpose. In the definition of the model, the influence of different parameters related to the aluminium packaging production and to the whole waste management system was taken into account.

The model is primarily based on the following four parameters:

- amount of commercialized aluminium packaging;
- gross MSW production;
- overall separated collection level;
- capacity of waste-to-energy plants.

Other minor variables are included, as summarised in Table 3.1. The model framework is illustrated in Figure 3.1: first of all, the waste collected with the separated collection and the aluminium packaging available on the market have been evaluated; then, knowing the amount of aluminium packaging in the separated collection and the quantity of non packaging aluminium in the URW, we have estimated the amount of aluminium in the residual waste. This aluminium is fed in part to incineration plants and in part to gasification plants, together with the URW. By considering also the aluminium content of the Refuse Derived Fuel (RDF), it is possible to evaluate the aluminium in the bottom ash produced during the combustion of URW and RDF and therefore the amount of aluminium recoverable and recyclable from the bottom ash.

The proposed model was applied to the Italian situation with a time perspective of about 10 years.

For each variable, one or more evolution scenarios were defined to estimate its values in years 2015 and 2020. The number of scenarios applied to each variable is reported in Table 3.1, whereas a brief description of each scenario is given below. The values which have been predicted for the model variables for 2015 and 2020 are summarized in Table 3.1 and compared with their value in 2009.

Table 3.1. Predicted values for the model variables.

ID	Variable description	number of scenarios	Scenario	units	2009*	2015	2020
A	Commercialized aluminium packaging	2	moderate growth	tonne year^{-1}	121,086**	128,535	135,092
			high growth	tonne year^{-1}	125,272**	145,526	162,358
B	Gross MSW production	2	moderate growth	10^6 tonne year^{-1}	31.88	33.21	33.48
			high growth	10^6 tonne year^{-1}	31.88	34.53	36.58
C	Separated collection level	1	-	%	33.6	41.7	48.7
D	Aluminium packaging in the separated collection	1	-	%	0.40** (0.29*)	0.35	0.31
E	Aluminium in RDF	1	-	%	0.6	0.6	0.6
F	Non-packaging aluminium in residual waste	1	-	%[a]	32.8	32.8	32.8
G1	URW to incineration plants	2	Base scenario	10^3 tonne year^{-1}	5,621	7,578	8,039
			Optimistic scenario	10^3 tonne year^{-1}	5,621	9,841	10,702
G2	URW to gasification plants	1	-	10^3 tonne year^{-1}	240	240	240
H1	RDF to incineration plants	1	-	10^3 tonne year^{-1}	553	951	1,468
H2	RDF to gasification plants	1	-	10^3 tonne year^{-1}	115	572	572
I1	Aluminium recovery efficiency from incineration bottom ash (Aluminium recovery and recycling efficiency from incineration bottom ash)	1	-	%[b]	32 (22)	32 (22)	32 (22)
I2	Aluminium recovery efficiency from gasification bottom ash (Aluminium recovery and recycling efficiency from gasification bottom ash)	1	-	%[b]	42 (32)	42 (32)	42 (32)

* True value

**Predicted value

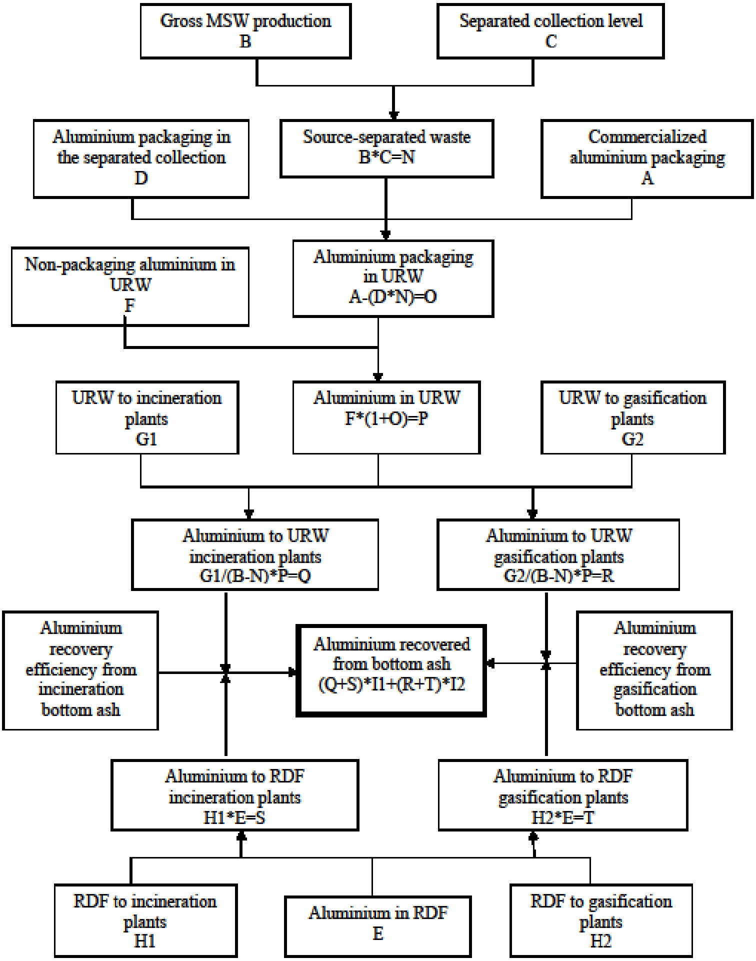


Figure 3.1. Model framework for the calculation of the amount of aluminium recoverable from the bottom ash.

Commercialized aluminium packaging

The use of aluminium packaging has increased in the last years, thanks to the properties of this material. The growing attention towards the environment has promoted the development of new technologies for packaging production, reducing their weight and the use of natural resources. For example, the thickness of beverage cans decreased by 6.9% from 1997 to 2007 and their weight decreased by 5.58% in the same period.

Based on these considerations, two scenarios for the evolution of aluminium packaging available on the market were considered: a high and a moderate growth scenario.

The former (i.e. high growth scenario) results from the projection of data of aluminium packaging commercialised in Italy between 2000 and 2007 and is based on a logarithmic curve to fit the data. The logarithmic function considers, on the one hand, the increase in the request of disposable packaging and, on the other, the reduction of the packaging weight as well as the possibility of the introduction in Italy of an environmental tax on those disposable products that are currently not subjected to any tax (e.g. aluminium foil).

The second scenario (i.e. moderate growth scenario) assumes a yearly growth rate of 1% for the commercialized aluminium packaging and it is therefore representative of an economic situation of low growth and moderate consumption.

The two scenarios are represented in Figure 3.2.

A clarification must be done: when referring to aluminium packaging we mean not only “true” packaging but also all similar items which are not formally considered packaging and then not submitted to the environmental tax, such as the household foil (aluminium foil and poly-laminated foil).

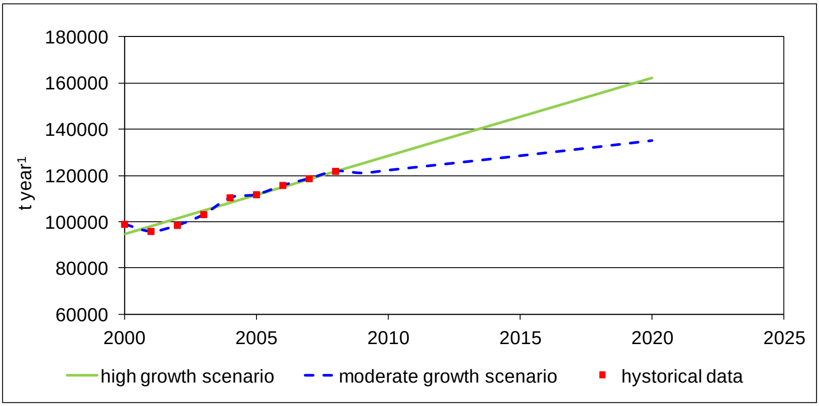


Figure 3.2. Representation of the two scenarios for the commercialised aluminium packaging.

Gross MSW production

The amount of MSW was calculated as the product of the resident population (medium scenario of ISTAT, 2009) and the per capita MSW production. For this variable, two scenarios were hypothesised: a moderate growth scenario and a high growth one.

For the first one (i.e. moderate growth scenario), the MSW per capita production from 2000 to 2009 was interpolated on a 3-parameter-exponential function (equation 3.1):

$$\mathrm{Pr}\,oduction_{MSWpercapita}(y) = A*(1-\exp^{-k(y-y^0)}) \qquad \text{(Eq. 3.1)}$$

where y indicates the time (year), A is the asymptotic value, k is the flexure parameter and y^0 is the translation parameter. The curve is reported in Figure 3.3 and shows that waste production stabilises around 540 kg year^{-1} per capita, as some Europeans countries have already stabilised their MSW production at around 500-550 kg year^{-1} per capita (EEA, 2011). This model considers the future effects of European policies aimed at the reduction of MSW production, or at least at its stabilisation (Directive 2008/98/EC).

The second scenario (i.e. high growth scenario) assumes a 1% yearly growth rate in MSW per capita production (Figure 3.3).

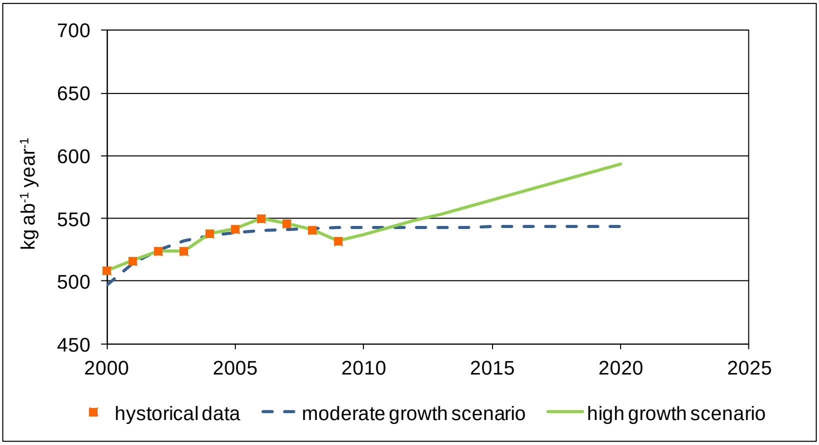


Figure 3.3. Representation of the two scenarios for gross MSW production.

Separated collection level

The evolution of the level of the separated collection until 2020 was obtained by interpolating the historical data from 2000 to 2009 (ISPRA, 2011), on the exponential function of Equation 3.1, in which the asymptotic value A is set to 100%. In this way, the predicted value of separated collection level for the year 2020 is very close to the 50% target prescribed by the European Directive 2008/98/EC. The curve is reported in Figure 3.4.

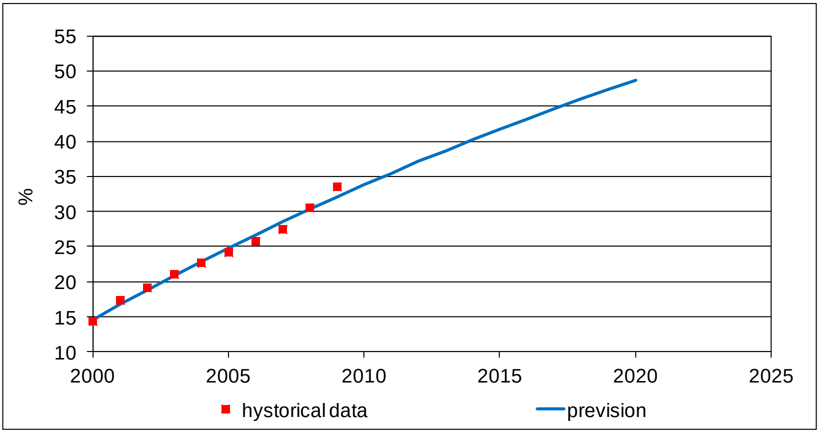


Figure 3.4. Prevision of the evolution of the separated collection.

Aluminium packaging in the separated collection

The content of aluminium packaging in the separated collection has been estimated with a linear interpolation of the historical data from 2002 to 2008, evaluated as the ratio between recycled aluminium and separated collection of MSW (ISPRA, 2011). Data for years 2000 and 2001 were disregarded, as they do not seem to match the overall trend, and also the datum for year 2009 was not considered, because an anomalous decrease of the amount of aluminium collected at the source was observed (CiAl, 2009).

The results show that in the next 10 years, the percentage of aluminium in the whole separated collection will most likely decrease (Figure 3.5). This can be explained if one considers that the separated collection of packaging is carried out extensively in Italy but it is not sufficient to achieve the target established by national and European legislations. To achieve these targets, the separated collection of the organic fractions of MSW has to play a major role, and as a consequence this will lead to a decrease of the relative amount of packaging materials in the separated collection in the coming years.

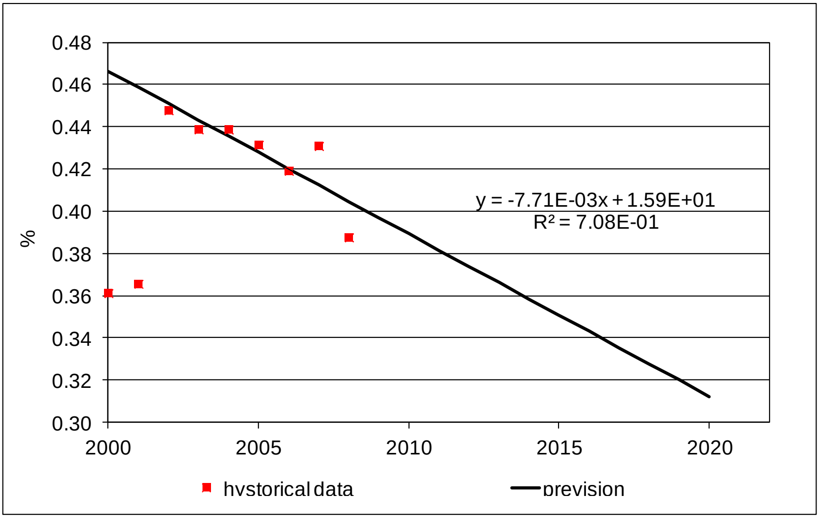


Figure 3.5. Prevision of the evolution of the presence of the aluminium packaging in the separated collection.

Aluminium in RDF

The presence of aluminium in RDF depends on the technology used in mechanical-biological plants utilised for RDF production. For simplicity, a constant value of 0.6% has been assumed, based on 34 average data from full-scale plants operating in Italy (data supplied by CiAl).

Non-packaging aluminium in unsorted residual waste

In URW, not only aluminium packaging but several other aluminium items, such as pots and coffee-pots, may be found. The contribution of such items is difficult to quantify, due to the heterogeneity of MSW.

In this work, a constant ratio of 32.8% of non-packaging aluminium over aluminium packaging has been assumed, based on the results obtained in three analyses that were carried out by the author on the residual waste sent to a waste-to-energy plant located in Northern Italy in 2009.

Waste-to-energy plants capacity

In 2009, 49 waste-to-energy plants were operating in Italy (ISPRA, 2011).

The capacity of incineration and gasification plants in 2015 and 2020 was estimated by adding, to the capacity installed in 2009, the capacity of new plants that are likely to be built in Italy, according to the Regional waste management plans. For simplicity, the waste-to-energy plants were classified in two groups: those that treat URW and those that treat RDF.

Two scenarios were considered: a base and an optimistic scenario.

The base scenario considers only those plants whose entry into operation by year 2020 is considered quite likely. The list of these plants is reported in Table 3.2.

The optimistic scenario considers all the plants planned by the regional waste management plans, also the ones whose construction is more uncertain. For example, the plants planned in Sicily, whose building company went bankrupt and for which Mafia infiltration is suspected; Greve plant, whose administrative procedure was interrupted by TAR verdict, etc. The list of these plants is reported in Table 3.3.

Table 3.2. WTE plants operating in 2009 and that will be operating in 2020 for the base scenario. In white the plants that burn MSW, in gray the plants that burn RDF (Data origin: regional MSW management plans, Federambiente, ISPRA).

Region	**City**	**Operating in 2009 (Yes/No) or data of starting**	**Capacity in 2009[a] (t $year^{-1}$)**	**Region**	**City**	**Operating in 2009 (Yes/No) or data of starting**	**Capacity in 2009[a] (t $year^{-1}$)**
Val D'Aosta	-	until 2015	80,000	Emilia Romagna	Granarolo dell'Emilia	Yes	198,384
Piemonte	Mergozzo	Yes*	30,099	Emilia Romagna	Ravenna	Yes	42,801.8
Piemonte	Torino Gerbido	2010	421,000	Emilia Romagna	Coriano	Yes	69,795.4
Piemonte	Vercelli	Yes	73,109	Emilia Romagna	Forlì	Yes	118,303.4
Piemonte	Novara-Verbania Cusio Ossola	until 2015	70,000	Emilia Romagna	Parma	2012	130,000
Lombardia	Cremona	Yes	69,795.6	Emilia Romagna	Piacenza	Yes	118,506.3
Lombardia	Busto Arsizio	Yes	136,350	Liguria	Genova Scarpino	until 2015	330,000
Lombardia	Como	Yes	69,500	Toscana	Livorno	Yes	47,907.7
Lombardia	Milano	Yes	518,733.3	Toscana	Rufina Selvapiana	Yes	7,838
Lombardia	Brescia	Yes	679,444.6	Toscana	Arezzo San Zeno	Yes	36,853
Lombardia	Bergamo	Yes	53,141.2	Toscana	Montale Agliana	Yes	32,643
Lombardia	Desio	Yes	44,415.2	Toscana	Ospedaletto	Yes	44,808.6
Lombardia	Sesto S. Giovanni	Yes	75,582.7	Toscana	Castelnuovo di Garfagnana	Yes	10,156.3

Table 3.2. (follow) WTE plants operating in 2009 and that will be operating in 2020 for the base scenario. In white the plants that burn MSW, in gray the plants that burn RDF (Data origin: regional MSW management plans, Federambiente, ISPRA).

Region	**City**	**Operating in 2009 (Yes/No) or data of starting**	**Capacity in 2009^a (t year^{-1})**	**Region**	**City**	**Operating in 2009 (Yes/No) or data of starting**	**Capacity in 2009^a (t year^{-1})**
Lombardia	Corteolona	Yes	65,122.6	Emilia Romagna	Ferrara Canal Bianco	Yes	132,597
Lombardia	Parona	Yes	242,018.6	Emilia Romagna	Reggio Emilia	Yes*	56,447
Lombardia	Trezzo d'Adda	Yes	175,236.5	Toscana	Poggibonsi Pian dei Foci	Yes	45,948.6
Lombardia	Dalmine	Yes	150,222.9	Toscana	Pietrasanta loc. Falascaia	Yes	21,024.5
Lombardia	Valmadrera	Yes	121,768.4	Toscana	Rufina Selvapiana	Plant enlargement 2012	67,000
Trentino Alto Adige	Bolzano	Yes	65,237	Toscana	Case Passerini	2012	132,000
Veneto	Padova	Yes	80,752	Marche	Tolentino	Yes	19,082.2
Veneto	Verona	Yes	135,700	Lazio	S. Vittore del Lazio	Yes	77,600.6
Veneto	Schio	Yes	73,249	Lazio	Albano	until 2020**	292,000
Veneto	Venezia Fusina	Yes	45,151	Lazio	Colleferro	Yes	3,062
Friuli Venezia Giulia	Trieste	Yes	159,378.3	Lazio	Colleferro	Yes	3,577.8
Emilia Romagna	Modena	Yes	137,010.7	Campania	Acerra	2009	239,602
Emilia Romagna	Modena	Plant enlargement until 2010	240,000	Campania	Salerno	until 2020**	450,000

Table 3.2 (follow). WTE plants operating in 2009 and that will be operating in 2020 for the base scenario. In white the plants that burn MSW, in gray the plants that burn RDF (Data origin: regional MSW management plans, Federambiente, ISPRA).

Region	**City**	**Operating in 2009 (Yes/No) or data of starting**	**Capacity in 2009[a] (t year^{-1})**
Campania	Santa Maria la Fossa	until 2015	406,000
Puglia	Massafra	Yes	88,829
Puglia	Statte	No	102,000
Puglia	Manfredonia	until 2020**	135,000
Puglia	Modugno	until 2020**	90,000
Basilicata	Melfi	Yes	54,441
Basilicata	Potenza	No	
Calabria	Gioia Tauro	Yes	114,190.1
Calabria	Gioia Tauro	Doubling of the plant until 2015	150,000
Sicilia	Messina	Yes	18.583
Sardegna	Capoterra	Yes	166,046.4
Sardegna	Macomer	Yes	29,264.6
Sardegna	Cagliari	2012	39,000
Sardegna	Fiumesanto	2012	125,500

[a] If the datum about the amount of waste treated in 2009 is not available. The datum about the authorised capacity is used. For the planned plants, the design capacity is used.

* The plant is currently working but it will be decommissioned until 2015

**Since it is difficult to define the startup data of the plant, it is supposed that it will be operating in 2020.

Table 3.3. Further plants considered in the optimistic scenario. (Data origin: regional MSW management plans, Federambiente, ISPRA).

Region	**City**	**Operating in 2009 (Yes/No) or data of starting**	**Capacity in 2009a (t year-1)**
Piemonte	Torino	2020	274,000
Toscana	Greve	until 2020	66,000
Umbria	Terni	No	60,000
Campania	Napoli	until 2015	400,000
Sicilia	Augusta	until 2015	405,848
Sicilia	Casteltermini	until 2015	272,466
Sicilia	Palermo	until 2015	536,665
Sicilia	Messina-Paternò	until 2015	648,000

Aluminium recovery (and recycling) efficiency from bottom ash

The recovery efficiency of the aluminium scraps from the bottom ash is usually evaluated considering those separated through ECS. This value is on interest for the bottom ash treatment plants, since it represents the amount of scraps that can be sold on the market.

From a material recovery point of view, it is more interesting to consider the amount of aluminium that can be recovered and truly recycled from the bottom ash. This value can be named "recovery and recycling efficiency" and includes the efficiency of the melting process in the secondary foundry.

In the present research the two efficiencies were considered:

- recovery efficiency of the aluminium scraps from the bottom ash: it was assumed equal to 32% of the aluminium fed to the incineration plants and 42% of that fed to gasification ones.
- recovery and recycling efficiency of the aluminium scraps from the bottom ash: it was assumed equal to 22% of the aluminium fed to incineration plants and 32% of the aluminium fed to gasification one.

The values for incineration plants refer to the results of the study presented in Chapter 4. The values for gasification plants assume that metal extraction is more efficient than for incineration bottom ash, due to a lower metal oxidation (Viganò et al., 2010).

Based on the results of the research reported in Chapter 4, only 21-23% of the aluminium in the URW can be recovered from the bottom ash and then recycled as secondary aluminium, also when the bottom ash is treated including a grinding stage and more than one screening stages. The value corresponds to a separation efficiency from the bottom ash equal to 26-37%, evaluated including the amount of aluminium trapped in the salt dross during the recycling process. These values refer to the situation characteristic of Northern Italy, where the separated collection is well established. In the South, where the source separation efficiency is modest, the percentage of aluminium recoverable from the bottom ash might be higher. However, considering that most of the incineration plant are located in the North of our country, these data were assumed for the whole Italy.

As commented in Chapter 2, data reported in the literature for aluminium recovery from the bottom ash (Table 2.3) are difficult to interpret, and can be only partially compared with the results obtained in this thesis and reported in Chapter 4. In Italy, the efficiency of the separated collection of metals is high (8.6 kg per capita in a year), especially in the North, and most of the aluminium in the residual waste probably consists in flexible packaging material. This type of material concentrates in the fine fraction of the bottom ash, where it is highly oxidised, and its recovery is quite poor.

3.2. RESULTS

The resulting ranges of the amount of aluminium that can be recovered from bottom ash in Italy in the years 2015 and 2020 are reported in Table 3.4 and represented in Figure 3.6.

Data reported in Table 3.5 and depicted in Figure 3.7 include the efficiency of the recycling process, then giving the amount of secondary aluminium potentially producible.

If we consider only the incineration plants whose construction is more probable (base scenario), between 16,300 and 20,000 tonnes of aluminium can be recovered in 2015 and between 19,300 and 27,300 tonnes in 2020. Of this amount, 14,300-18,000 tonnes in 2015 and 17,300- 25,000 tonnes in 2020 come from URW and RDF incineration plants and 1,900-2,100 tonnes in 2015 and 2,000- 2,300 tonnes in 2020 come from gasification plants. This corresponds to an amount of aluminium recoverable and recyclable from the bottom ash included between 11,300-14,000 tonnes in 2015 and between 13,400-19,000 tonnes in 2020. Of this amount, about 9,900-12,400 tonnes in 2015 and about 11,900-17,200 tonnes in 2020 come from incineration plants and the residual from gasification plants.

Considering also the plants whose construction is less probable (optimistic scenario), the amount of aluminium potentially recoverable from the bottom ash increases at 20,000-24,900 tonnes in 2015 and 24,100- 34,600 tonnes in 2020, of which 18,000- 22,800 tonnes in 2015 and 22,100-32,300 tonnes in 2020 are recovered from incineration plants and the rest from gasification plants. The aluminium potentially recoverable and recyclable from the bottom ash amounts at 13,900-17,300 tonnes in 2015 and 16,700- 24,000 tonnes in 2020.

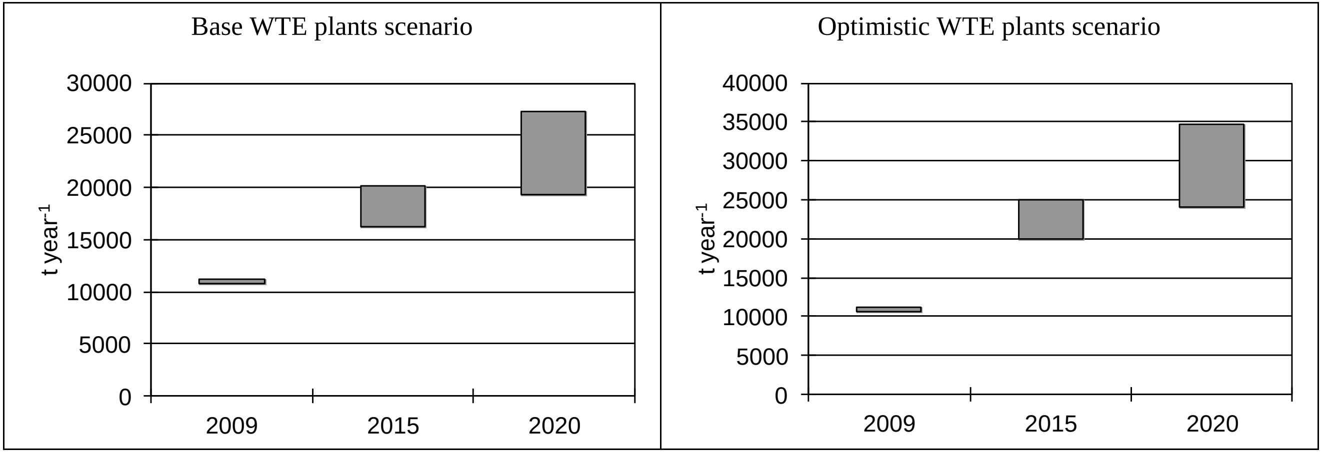
In both cases, the upper boundary of the range corresponds to a situation of ‘moderate’ growth in MSW production and of ‘high’ growth in commercialized aluminium packaging; the lower boundary corresponds to the opposite situation, i.e. ‘high’ growth of MSW production and ‘moderate’ growth in commercialized aluminium packaging. The aluminium recovered from incineration and from gasification bottom ash is reported separately because bottom ash from gasification plant are most likely vitrified and require a different treatment compared to those from incineration. In addition, metal scraps from gasification bottom ash are much less oxidised compared to that from incineration plants.

Table 3.4. Aluminium recoverable from bottom ash (t year^{-1}).

Plant	WTE plants scenario	2009	2015	2020
Incineration	base	9,932-10,404	14,322-17,965	17,302-25,002
	optimistic	9,932-10,404	18,051-22,782	22,096-32,346
Gasification		789-815	1,967-2,119	2,015-2,316
total	**base**	**10,721-11,219**	**16,289-20,084**	**19,317-27,318**
	optimistic	**10,721-11,219**	**20,018-24,901**	**24,111-34,662**

Table 3.5. Aluminium recoverable and recyclable from bottom ash (t year^{-1}).

Plant	WTE plants scenario	2009	2015	2020
Incineration	base	6,828-7,153	9,846-12,351	11,895-17,189
	optimistic	6,828-7,153	12,410-15,663	15,191-22,238
Gasification		601-621	1,498-1,614	1,535-1,765
total	**base**	**7,429-7,774**	**11,344-13,965**	**13,430-18,954**
	optimistic	**7,429-7,774**	**13,908-17,277**	**16,726-24,003**


Base WTE plants scenario

Optimistic WTE plants scenario

Figure 3.6. Aluminium recoverable from the bottom ash in Italy in 2015 and 2020.

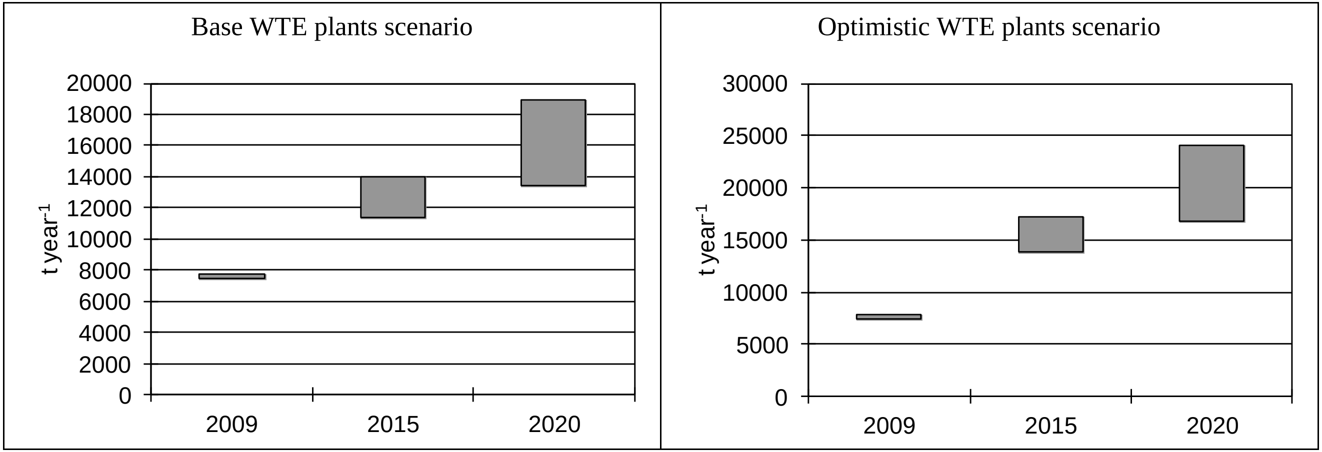


Figure 3.7. Aluminium recoverable and recyclable from the bottom ash in Italy in 2015 and 2020.

Some considerations need to be made on the probability associated to the different scenarios displayed in Tables 3.6, 3.7, 3.8 and 3.9. For example, the base scenario for waste incineration plants is considered more probable, taking into account the typical Italian situation. Regional waste management plans seem, in fact, quite ambitious and it is difficult to believe that all the planned plants will actually be into operation as for 2020. If we consider the base scenario for the incineration plants, the scenario of high growth of commercialized aluminium packaging and of moderate growth of MSW production seems the most probable, since it describes the natural evolution of the historical data. Scenarios with the same growth rate of MSW and of commercialized aluminium packaging can be considered quite probable, especially the one which considers a moderate growth for both MSW and commercialized aluminium, due to the economical crisis which is decreasing overall consumptions. On the contrary, the scenario of moderate growth of commercialized aluminium packaging and high growth of MSW production is far less probable, because it describes a situation in which the total consumption of packaging grows quicker than that of the aluminium packaging, whereas, in recent years, aluminium has acquired a relevant share of the packaging market, thanks to its favourable technical properties (Schiona, 2009).

Based on these considerations, the range of the amount of aluminium which is more likely to be recovered from bottom ash narrows between 17,100 and 20,000 tonnes in 2015, and between 21,700 and 27,300 tonnes in 2020. This corresponds to an amount of secondary aluminium potentially producible included between 11,900 and14,000 tonnes in 2015 and between 15,000 and 19,000 tonnes in 2020.

All the estimates conducted so far refer to the sole amount of aluminium. As this metal is extracted with ECS together with other non ferrous metals and assuming a 60% content of aluminium in the mixture, then the most likely value of non-ferrous metals recoverable from bottom ash is 28,600-33,500 tonnes in 2015 and 36,000- 45,500 tonnes in 2020. The most likely amount of non-ferrous metals recoverable and recyclable from the bottom ash thus narrows between 20,000 and 23,300 tonnes in 2015 and between 25,000 and 31,600 tonnes in 2020.

Bottom ash production in 2015 and 2020, evaluated considering that bottom ash account on average for 20% of the URW and 3.5% of RDF, is reported in Table 3.10. The upper boundary of the range corresponds to the optimistic incineration scenario; the lower boundary corresponds to the base incineration scenario.

Table 3.11 reports the bottom ash treatment plants actually installed in our Country or that will be operating soon (incomplete list). Despite the lack of information, we can notice that the plants currently installed or soon available is insufficient to treat all the bottom ash produced in 2015 and 2020. It is, therefore, evident the possibility to improve metals recovery from the ash by increasing the treatment capacity installed in our Country.

Table 3.6. Aluminium recoverable from MSW and RDF incineration bottom ash (t $year^{-1}$).

Scenario			2009	2015	2020
Base WTE plants scenario	High growth commercialised aluminium packaging	Moderate growth MSW production	10,404	17,965	25,002
		High growth MSW production	10,404	17,042	22,266
	Moderate growth commercialised aluminium packaging	Moderate growth MSW production	9,932	15,138	19,579
		High growth MSW production	9,932	14,322	1,7302
Optimistic WTE plants scenario	High growth commercialised aluminium packaging	Moderate growth MSW production	10,404	22,782	32,346
		High growth MSW production	10,404	21,583	28,703
	Moderate growth commercialised aluminium packaging	Moderate growth MSW production	9,932	19,110	25,126
		High growth MSW production	9,932	18,051	22,096

Table 3.7. Aluminium recoverable from MSW and RDF gasification bottom ash (t $year^{-1}$).

Scenario		2009	2015	2020
High growth commercialised aluminium packaging	Moderate growth MSW production	815	2,119	2,316
	High growth MSW production	815	2,080	2,209
Moderate growth commercialised aluminium packaging	Moderate growth MSW production	789	2,001	2,104
	High growth MSW production	789	1,967	2,015

Table 3.8. Aluminium recoverable and recyclable from MSW and RDF incineration bottom ash (t year^{-1}).

Scenario			2009	2015	2020
Base WTE plants scenario	High growth commercialised aluminium packaging	Moderate growth MSW production	7,153	12,351	17,189
		High growth MSW production	7,153	11,716	15,308
	Moderate growth commercialised aluminium packaging	Moderate growth MSW production	6,828	10,407	13,460
		High growth MSW production	6,828	9,846	11,895
Optimistic WTE plants scenario	High growth commercialised aluminium packaging	Moderate growth MSW production	7,153	15,663	22,238
		High growth MSW production	7,153	14,838	19,733
	Moderate growth commercialised aluminium packaging	Moderate growth MSW production	6,828	13,138	17,274
		High growth MSW production	6,828	12,410	15,191

Table 3.9. Aluminium recoverable and recyclable from MSW and RDF gasification bottom ash (t year^{-1}).

Scenario		2009	2015	2020
High growth commercialised aluminium packaging	Moderate growth MSW production	621	1,614	1,765
	High growth MSW production	621	1,585	1,683
Moderate growth commercialised aluminium packaging	Moderate growth MSW production	601	1,525	1,603
	High growth MSW production	601	1,498	1,535

Table 3.10. Prevision of the production of bottom ash from WTE plants (t year^{-1}).

Plant	**Treated waste**	**2009**	**2015**	**2020**
Incineration	URW	1,124,252	1,515,527-1,968,123	1,607,707-2,140,303
	RDF	19,343	33,285	51,380
Gasification	URW	48,000	48,000	48,000
	RDF	4,032	20,003	20,003
Total		1,195,627	1,616,815-2,069,411	1,727,090-2,259,686

Table 3.11. Bottom ash treatment plants in Italy.

Plant	**Place**	**Operating (Yes/No) or startup date**	**Capacity (t year^{-1})**	**Bottom ash treatment**
Ecodeco	Lacchiarella	Yes	120,000	• Ferrous and non-ferrous metals recovery • Inert material to road construction
BSB	Noceto	Yes	50.,000	• Ferrous and non-ferrous metals recovery • Inert material to concrete production
ENIA	Piacenza	No (project currently stopped)	30,000	• Ferrous and non-ferrous metals recovery • Inert material to clinker production
HERA	Modena	test	30,000 (capacity of 80,000)	• Ferrous and non-ferrous metals recovery • Inert material to road construction
IRIS	Conselve	Yes	150,000	• recupero metalli ferrosi e non ferrosi • Recovery of the inert material
Appia Energy	Massafra	Yes	5,000	n.a.
TMR	Torino	Planning stage	n.a.	n.a.
Furia srl	Fidenza	n.a.	n.a.	n.a.
Officina dell’ambiente	Lomello	Yes	120,000	n.a.

Table 3.11. **(follow)** Bottom ash treatment plants in Italy.

Plant	**Place**	**Operating (Yes/No) or startup date**	**Capacity (t year^{-1})**	**Bottom ash treatment**
Cologne Asfalti	Cologne	Yes	20,000	• Ferrous metals recovery • Inert material to clinker production
Trezzo incinerator	Trezzo	Planning stage	70,000	• Ferrous and non-ferrous metals recovery • Inert material to concrete and clinker production ("Superpozzolana")
RMB	Polpenazza del Garda	Yes	n.a.	• Ferrous and non-ferrous metals recovery • Inert material to clinker production and road construction
PBR	Maclodio	Yes	35,000*	• Washing and stabilisation of the bottom ash • metal recovery
SADI	Orbassano	Yes	120,000*	• Ferrous metals recovery • Inertisation of the ash with cement
Eco.nova	Brescia	Yes	n.a.	n.a.
TOTAL**			750,000	

*including other waste treated in the plant

**The capacity of the TMR and Furia plants is not considered, since the data are not available. Furthermore the list of the plants is not complete.

4. ALUMINIUM OXIDATION IN THE FURNACE OF WTE PLANTS

Ferrous and non ferrous metal scraps are increasingly recovered from municipal solid waste incineration bottom ash and used in the production of secondary steel and aluminium. However, during the incineration process, metal scraps contained in the waste undergo oxidation processes, which determine a loss of their recoverable mass. This chapter presents the results of a research carried out on two different incineration plants located in Northern Italy to evaluate the behaviour of different types of aluminium packaging materials during standard operation. Their partitioning and oxidation level in the residues of the incineration process were evaluated, together with the amount of potentially recoverable aluminium. At the same time, the partitioning and the oxidation level of the aluminium naturally presented in the URW were evaluated, in order to have information not only on some specific packaging materials but on aluminium in general, including also the non-packaging aluminium in the waste.

4.1. MATERIALS AND METHODS

The research was carried out on two incineration plants and consisted in 7 experimental tests, during which the behaviour of rigid and flexible aluminium packaging was investigated. The list of the experimental tests is reported in Table 4.1.

Table 4.1. List of the experimental tests.

Incineration plant	Test	Data	Packaging material
Valmadrera	#1	6-6-11	Beverage cans
	#2	7-6-11	Trays
	#3	8-6-11	Spray cans
	#4	13-7-11	Mix aluminium foil and poly-laminated foil
Piacenza	#5	30-1-12	Spray cans
	#6	31-1-12	Aluminium foil
	#7	1-2-12	Paper-laminated foil

Plants description

Valmadrera incineration plant consists of two treatment lines, line 1 and line 3, with a throughput of about 6 and 9.5 tonnes per hour of waste, respectively. The experimentation was conducted on line 3. The feeding includes urban, urban-like non hazardous waste and hospital waste (about 8% of the total waste feed), the latter not fed to the furnace during the experimentation due to the impossibility to accurately reconstruct its composition. The plant is equipped with a forward-acting grate and a wet discharge system for the bottom ash. The grate is divided into four sections whose movement can be regulated independently. The secondary air feeding is regulated to maintain the temperature above 850°C for at least 2 seconds, and the oxygen concentration in the flue gas at around 6%. A fraction of the clean flue gas (about 15%) collected downstream the fabric filter is recirculated in the post-combustion chamber, in order to reduce NOx formation and to increase the steam production. The plant is equipped with a waste heat boiler for combined heat and power (CHP) production through a steam turbine. Flue gas treatment configuration is based on a dry-wet integrated process design and includes a dry stage for the removal of acid gases and micro- pollutants with the injection of sodium bicarbonate and activated carbon; a filtration stage with a fabric filter operating at 180°C; a catalytic reactor with ammonia injection for the removal of NOx (SCR) and dioxins and a wet scrubber with water and soda injection to complete the removal of the acid gases and the most volatile heavy metals, such as mercury.

Piacenza incineration plant consists of two identical treatment lines, with a throughput of about 7.5 tonnes per hour of waste each. All tests were conducted on line 2. The typical feeding includes urban, urban-like non hazardous waste, sewage sludge and hospital waste, the latter not fed to the furnace during the experimentation. The waste bunker has a capacity of 3500 m^3 and it is used for urban and urban-like waste, whereas the hospital waste is directly fed to the hopper of the furnace through an automated system based on the use of single boxes. The same system was used to feed the tested aluminium packaging in the furnace.

The furnaces are equipped with a backward-acting grate (supplied by Martin GmbH) divided into four sections, whose movement can be regulated independently. Primary air is fed from underneath the grate. At the end of the grate, the bottom ash falls down in a water bath, where it is quenched. The extraction system is designed to decrease the moisture content of bottom ash, thanks to its “squeezing” in the discharge slide; the final moisture content of bottom ash is in fact quite low, and included between 12 and 18%. The bottom ash is then discharged on a conveyor belt, where a magnet removes the big ferrous scraps.

The plant is equipped with a waste heat boiler for combined heat and power (CHP) production through a steam turbine. Flue gas configuration is based on a dry process design and includes a first injection of ammonia and of a sorbent (Depurcal MG®) in the combustion chamber to remove part of the NOx and acid gases; a high-dust catalytic reactor to complete the removal of NOx; an electrostatic precipitator (ESP); the injection of lime and activated carbon to complete the removal of the acid gases and of the micro-pollutants and a final stage of filtration with a fabric filter (FF).

Field tests

The characteristics of the tested packaging materials are reported in Table 4.2. It is important to notice that the beverage cans and the spray cans used in Piacenza test were post-consumer and thus they probably contained organic and/or inorganic impurities, whereas for the other packaging (trays and foils) pre-consumer materials were used, due to the technical impossibility to recover a sufficient amount of selected post-consumer material from the separated collection. The actual amount of aluminium fed to the furnace was evaluated considering the alloy composition of each type of packaging and the structure and composition of poly-laminated foils.

The packaging materials were mixed with the waste in order to increase its content of aluminium and the resulting doped waste was fed to the furnace in about 1-2 hours.

For what concerns Valmadrera plant, during the first three tests devoted to rigid aluminium packaging items (beverage cans, spray cans and trays,) about 240 kg of aluminium were mixed with about 8,000 kg of residual waste ready to be incinerated, whose characteristics are reported in Table 4.3. During the last test carried out in Valmadrera plant on flexible packaging (a mix of aluminium foil and poly-laminated foil), the amount of packaging increased at 979 kg, which were mixed with about 30,000 kg of residual waste. The mixing took place in a dedicated bunker section, which was previously emptied, and it was performed with the help of the grab in order to make the charge homogeneous. This doping operation was carried out with the aim to increase the aluminium content in the residual waste from about 0.8% (background) to more than 3.5%.

The preparation of the waste charge was different in Piacenza plant. Three selected aluminium packaging charges were prepared, one for each type of packaging. Each charge was divided into 8-10 sub-charges and fed to the furnace by using the feeding system usually dedicated to the hospital waste. This system consisted in individual containers which were filled with the aluminium packaging and then automatically unloaded in the feeding hopper. The system was completely automated. The aluminium charge feeding took about 2 hours and the boxes were discharged every 10-12 minutes. A good mixing of the aluminium charge with the waste was guaranteed by alternating the feeding of the two materials in the feeding hopper. About 450-650 kg of packaging material was mixed with 7-14 tons of waste, increasing its aluminium content from about 1.7% to about 4.5-7.8% as reported in Table 4.4.

Table 4.2. Tested materials.

Test	Material	Characteristics
#1	Aluminium cans (post-consumer)	volume: 330 ml
		body alloy: 3104
		lid alloy: 5182
		body thickness: 0.09 - 0.15 mm
		lid thickness: 0.22 - 0.25 mm
		weight: 13.2 g
#2	Aluminium trays	dimension: 132x107xh30 mm
		alloy: 8006
		body thickness: 0.05 mm
		weight: 4.28 g
#3	Aluminium spray cans (test 3: pre-consumer test 5: post-consumer)	dimension: 50x156 mm
		alloy: 3000
		body thickness: 0.32 mm
#5		bottom thickness: 0.9 mm
		crown thickness: 0.44 mm
		weight: 25 g
#4	Aluminium packaging foil 1	alloy: 1200
		brown coloured
		thickness: 12 μm
	Aluminium packaging foil 2	alloy: 8079
		gold coloured
		thickness: 42 μm
	Aluminium poly-laminated packaging foil 1	alloy: 1200
		gold coloured
		thickness: 10 μm
		Poly-laminated with paper 30 gr m^{-2}
		with glue solvent 2 gr m^{-2}
	Aluminium poly-laminated packaging foil 2	protected aluminium
		alloy: 1200
		thickness: 10 μm
		Poly-laminated with paper 20 gr m^{-2} and polyethylene 9 gr m^{-2}
		with wax 11 gr m^{-2}

*post-consumer materials

Table 4.2. (follow) Tested materials.

Test	**Material**	**Characteristics**
#4	Aluminium poly-laminated packaging foil 3	Triplex foil Alu/Pe/Alu
		alloy: 1200
		thickness: 12/60/12 μm
		with solvent glue 2.5 gr m^{-2} per each side
	Aluminium poly-laminated packaging foil 4	protected aluminium
		alloy: 8079
		thickness: 38 μm
		Poly-laminated with polyethylene thickness 45 μm
#6	Aluminium packaging foil 1	alloy: AA1200
		gold coloured
		thickness: 12 μm
	Aluminium packaging foil 2	alloy: AA1200
		coloured
		thickness: 12 μm
	Aluminium packaging foil 3	alloy: AA1200
		printed
		thickness: 14 μm
#7	Aluminium paper-laminated packaging foil 1	alloy: AA1200
		coloured
		thickness: 12 μm
		Poly-laminated with tissue paper 25 g m^{-2}
	Aluminium paper-laminated packaging foil 2	alloy: AA1200
		thickness: 12 μm
		Poly-laminated with paper 25 g m^{-2}

Table 4.3. Composition of the residual waste incinerated in Valmadrera and Piacenza plants during standard operations.

Waste composition (%)	**Valmadrera**	**Piacenza**
Aluminium	0.73 ± 0.00	1.67 ± 1.08
Paper and paperboard	24.77 ± 4.31	31.68 ± 6.05
Plastic	23.22 ± 5.25	27.14 ± 6.66
Ferrous metal	2.13 ± 1.07	1.85 ± 1.59
Wood	1.16 ± 0.58	3.45 ± 2.91
Glass	1.45 ± 0.05	3.06 ± 2.09
Laminated	0.79 ± 1.40*	n.a.
Organic fraction	16.41 ± 5.85	13.37 ± 9.29
Green waste	5.47 ± 8.66	Included in the organic fraction
Textile	4.35 ± 1.76	7.07 ± 4.58
Inert fraction	1.97 ± 1.26	0.83 ± 1.65
Fines	5.14 ± 1.58	5.37 ± 4.30
Other waste (nappies, leather, non classifiable waste)	11.34 ± 3.48	3.11 ± 2.72
Hazardous waste	1.05 ± 0.34	0.49 ± 1.78
LHV (kJ kg^{-1})	15,391 ± 3471	14,207 ± 3,194

* The value includes aluminium.

Table 4.4. Doped waste fed into the furnace during the tests**.**

Test		**Aluminium packaging (kg)***	**MSW (t)**	**Other waste (t)**	**Total estimated aluminium content (%)***
#1	Beverage cans	240	8	0	3.7
#2	Trays	240	9.5	0	3.2
#3	Spray cans	240	7.6	0.14**	3.5
#4	Mix aluminium foil and poly-laminated foil	979	30.2	0	4.0
#5	Spray cans	500	14	1.8***	4.5
#6	Aluminium foil	448	7	1.2***	6.5
#7	Paper-laminated foil	635	8.4	1.1***	7.7

*Gross weight
**hospital waste
***sludge

Bottom and fly ash were sampled every 30 minutes on average, depending on the operating conditions of the plant, in order to sample both the bottom and fly ashes resulting from the URW usually burnt in the plant (blank samples) and those resulting from the doped waste. Sampling of bottom ash was intensified when its output started being affected by the doped waste input. Bottom ash was sampled from the conveyor belt in a quantity of about 5 kg per sample in the first tests on rigid packaging and collected in plastic buckets. This amount was increased to 10-15 kg during the tests devoted to aluminium flexible packaging and the second test on spray cans, carried out in Piacenza plant, because, following the preliminary results of the first tests, this turned out to be a critical aspect.

In Valmadrera plant all the fly ash was sampled together at its discharge in the big bags and collected in plastic pots of 1 l each. The boiler was regularly cleaned every 100 minutes; each cleaning cycle requires about 45 minutes. In Piacenza plant, on the contrary, boiler ash, ESP ash and FF ash were sampled separately from the redler transportation system, collecting the ash from the openings used for the maintenance.

During the tests in Piacenza, some samples of the quenching water of the bottom ash were taken from the quenching tank.

Aluminium potentially present in the flue gas at the stack was voluntarily neglected as a previous research study focusing on the balance of trace elements showed that it is negligible (Stucchi, 2003).

The mass of the incinerated waste and the resulting residues generated on average by the plant are summarized in Table 4.5.

Table 4.5. Incinerated waste and residues produced on average by Valmadrera and Piacenza plants.

Waste and residues		**Valmadrera (line3)**	**Piacenza (line 2)**		
MSW	t year^{-1}	37,119	34,456		
Urban like waste	t year^{-1}		21,704		
Hospital waste	t year^{-1}	3,137	990		
Sludge	t year^{-1}	0	2,075		
Bottom ash	t year^{-1}	7,558	11,282		
	kg t_{waste}^{-1}	187.3	190.5		
Fly ash	t year^{-1}	1,221	**Boiler ash***	t year^{-1}	952
				kg t_{waste}^{-1}	16.1
			ESP ash*	t year^{-1}	476
	kg t_{waste}^{-1}	30.7		kg t_{waste}^{-1}	8.0
			FF ash	t year^{-1}	1,228
				kg t_{waste}^{-1}	20.7

*The partitioning between Boiler ash and ESP ash is tentatively estimated by the plant operator

The residence time of the waste during the whole treatment (from the feeding hopper to the bottom ash extraction system) was evaluated *ex-post* by looking at the results of aluminium concentration analysis in bottom ash and it was found very variable and included between 4 and 6 hours for Valmadrera plant, depending on the plant operation, and 9-10 hours for Piacenza plant.

Samples analysis

The bottom ash was pre-treated according to the flow chart in Figure 4.1. It was first dried [1] and then screened at 0.8 mm [2]. The choice of 0.8 mm as cut dimension is due to the recycling capacity of aluminium secondary smelters. Particles bigger than 0.8 mm can generally be recycled, whereas those smaller than 0.8 mm cannot be recovered and determine a loss of material. Iron and inert scraps [3] and non-ferrous lumps [4] were manually sorted out. The fraction above 0.8 mm was grinded in a grindstone [5] in order to make its laboratory analysis possible and afterwards it was further screened at 0.8 mm [6]. In this way it was possible to isolate the coarse fraction (above 0.8 mm) rich of metals which, unlike the inert material, are not crushed in the grindstone but just flattened.

The two inert fractions below 0.8 mm (before and after the grinding) were analysed separately. In these fractions aluminium is present in low amount and the content of metallic aluminium was detected using caustic soda attack followed by the measurement of the volume of the produced hydrogen, while the content of total aluminium was evaluated with X-ray fluorescence spectroscopy (XRF) [7]. The analysis of the metallic aluminium using soda attack method is quite usual and reported in other papers (Hu et al., 2011; Aubert et al., 2004). The chemical reaction that controls the hydrogen production is given in Eq. 4.1:

$$2Al + 2OH^- + 2H_2O \rightarrow 2AlO_2^- + 3H_2 \qquad \text{(Eq. 4.1)}$$

The fraction above 0.8 mm resulting from the second screening underwent an iron sorting with magnet [8] and it was then melted with salt (70% NaCl and 30% KCl) in the crucible [9] together with the aluminium lumps manually sorted in the previous steps. The melting process was carried out in a smelter located in Northern Italy, following the standard procedure they normally use to evaluate the metallic Al content in the input scraps. However, the non-ferrous metals recovered from the bottom ash were melted all together, without a previous separation of the Al lumps from the other non-ferrous scraps. As this non-ferrous mix had a lower content of Al compared to the material usually treated in the smelter, the efficiency of the melting process performed during our investigation was lower than the true recycling efficiency of a melting furnace, where such low quality materials are usually diluted in a cleaner aluminium charge. The salt dross was

analysed with the same procedure as for the inert fraction of the bottom ash, whereas the recoverable metal ingot was analysed by an optic emission spectrometer (OES or quantometer), in order to evaluate its content of Al (all considered metallic) [10].
Some modifications in the procedure were introduced for the samples of the test on aluminium flexible packaging in Valmadrera and the three tests in Piacenza: the fraction above 0.8 mm resulting from the second screening, after iron sorting with the magnet, was screened again with a 5 mm mesh screen [11]. The fraction above 5 mm and the aluminium lumps manually sorted, consisting almost entirely of aluminium and other non-ferrous metals and representing non-ferrous metals that can be separated with a traditional Eddy Current Separator (ECS), were melted together to obtain the metal ingot. The fraction between 0.8 and 5 mm, representing the material that can be recovered only with advanced ECS, such as high frequency ECS, wet backward ECS, Magnus separator specifically calibrated, was melted separately and its dross analysed with soda attack and XRF.

Fly ash samples were directly analysed with soda attack and XRF in order to determine their contents of metallic and total aluminium, respectively ([7] in Figure 4.1).

The bottom ash quenching water, sampled during the tests in Piacenza plant, was analysed through inductively coupled plasma mass spectrometry (IPC-MS) to measure its concentration of total Al.

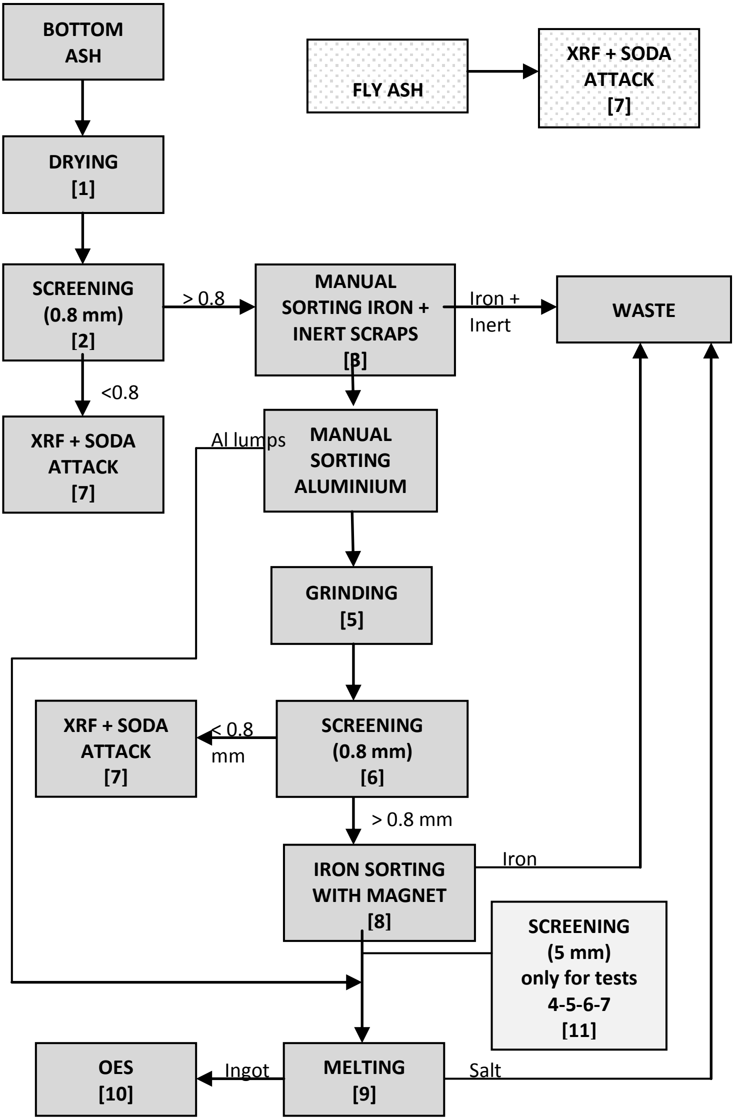
The tests in Piacenza saw some differences and improvements for what concerns samples analysis, compared to those in Valmadrera.

First of all, the laboratory device used to measure metallic aluminium content with the “soda attack” method was partially modified, by substituting the mercury column used for the pressure reading with a digital sensor for gas velocity and flow meter measurement (Flowtest ST by Tecora). This allowed for a better precision, and a consequent reduction of the standard deviation associated to the metallic Al measurement. In fact, the first instrument used for the soda attack method resulted characterised by a very low precision, with standard deviations on the analyses included between 0% and 72% of the average value, with the highest values referring to fly ash. By changing the pressure reading system, the deviation standard decreased to 5-25% of the average values. The method resulted, in any case, characterised by a low precision, probably due to the low concentration of metallic aluminium (especially in the fly ash) too closed to the detection limit of the instrument. Low precision levels were also observed by Aubert et al. (2004).

Second, the influence of the bottom ash drying process was evaluated by sampling a double amount of some samples and by drying half sample at ambient air and the other half on a common methane burner. The drying of all the samples was, in fact, carried out on a methane burner, in uncontrolled conditions, due to the huge number of samples and thus the impossibility to performed the drying in a oven with controlled atmosphere. As a general indication, the drying process on the methane burner increases the oxidation level of aluminium in the bottom ash fine fractions, both after the first and the second screening, of about 7 and 17%, respectively. For the salt dross, the behaviour is not univocal. In fact, the amount and oxidation level of aluminium in the salt dross in not due only to the characteristics of the aluminium lumps separated by the ash, but also to the melting process efficiency, which was performed manually and thus was characterised by an efficiency variable from one time to another. The results are reported in Table 4.6.

Table 4.6. Aluminium oxidation level (% value) in the samples dried open-air and on a methane burner.

test	**Drying process**	**Bottom ash fraction < 0.8 mm (1st screening)**	**Bottom ash fraction < 0.8 mm (2nd screening)**	**salt dross**
Spray cans	Methane burner	88	81	38
	ambient air	80	66	69
Aluminium foil	Methane burner	84	82	59
	ambient air #1	79	67	37
	ambient air #2	79	70	73



XRF: X-ray fluorescence spectroscopy
OES: optic emission spectrometer
Figure 4.1. Samples treatment and analysis.

Data processing

Data from the samples analysis were treated in order to exclude the contribution of the aluminium which is naturally present in the waste (background concentration) and, thus, to evaluate the mass balance of the aluminium packaging materials fed artificially to the furnace of the two incineration plants. First of all, the average total and metallic aluminium in the residues resulting from the non-doped waste was evaluated, for each residue and for each test, by averaging the corresponding values obtained by the analysis of the samples representative of the non-doped waste, namely those samples which lay outside the time period during which the effect of doping is clearly visible. Then the aluminium content in the residues representative of the doped waste was estimated by numerical integration of the concentration curve (aluminium % in the samples) during the time frame where the growth trend is located. Finally, the contribution ($kg_{Al}\ kg^{-1}_{residue}$ min) of the aluminium packaging fed to furnace was evaluated as the difference between the aluminium content in the residues representative of the doped waste and in that representative of the background residual waste as it is. The procedure is graphically represented in Figure 4.2.

The aluminium flow rate in the residues produced by the incineration process was then calculated by multiplying the contribution of the packaging in each fraction, evaluated as previously illustrated, by the corresponding flow rate properly converted into kg min^{-1}.

Data referred to the salt dross were considered only for the tests performed in Piacenza plant. On the contrary, for what concerns the packaging materials tested in Valmadrera, data on the salt dross were not included in the mass balance, since they did not reveal any significant variation between the samples representative of the non-doped waste and those representative of the doped waste. For the same reasons, also the aluminium that dissolved in the bottom ash quenching water was not included in the mass balance.

The average total and metallic aluminium in the residues resulting from the non-doped waste was used to calculate the mass balance of the mixed aluminium naturally presented in the URW.

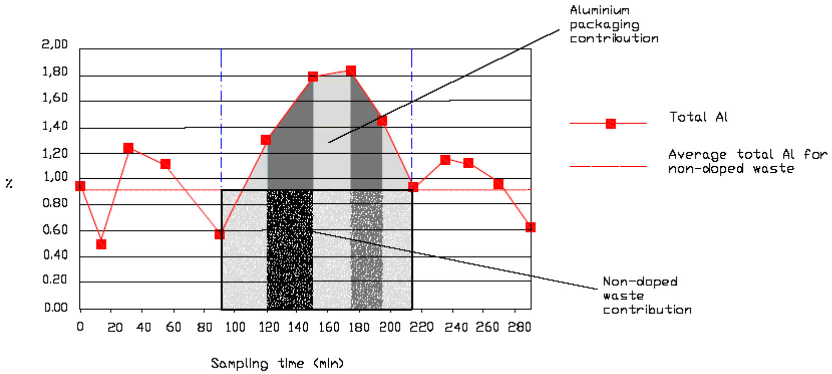


Figure 4.2. Example of numeric integration of the curve of total aluminium in fly ash.

4.2. RESULTS

4.2.2. Behaviour of the aluminium packaging materials

The chapter described the results of the tests carried out on selected aluminium packaging materials. The detailed analysis of the paper-laminated foil is reported in Annex I, as an example. The analysis of the other packaging materials was performed in the same way and, for this reason, it is not reported in the thesis.

Aluminium flow rate

The results of the tests are graphically represented in Figure 4.3. The Figure illustrates the partitioning of total aluminium in the residues of the incineration process. It is important to distinguish between the tests carried out in Valmadrera plant and that carried out in Piacenza. In fact, the two plants present some differences, especially for what concerns the grate and the bottom ash extraction system. In addition the sampling procedure and the samples analysis present some differences between the two campaigns. The figure reports also the results of the non-doped waste, which will be discuss in the next chapter.

Mass balance was evaluated by neglecting the amount of aluminium that fell through the grate and stuck on its surfaces. For Valmadrera tests, also the amount of aluminium that was not fed into the furnace but lost in the waste bunker was not considered.

Ingots fraction is representative of the metal actually recoverable from the bottom ash and, since it is the result of the melting process, this value includes also the efficiency of the actual recycling process. On the contrary, the aluminium in the other residues (fly ash, bottom ash below 0.8 mm before and after grinding) represents a loss, because it cannot be recovered. In fact, in both bottom ash fine fractions (below 0.8 mm before and after grinding), aluminium metal fragments are extremely small in size and their recovery is virtually impossible using the current ECS technology.

The amount of aluminium found in fly ash is below 7% for all the types of packaging; regardless of the peculiarities of each packaging or alloy, this amount is in any case negligible.

In contrast, data corresponding to the fine fractions (below 0.8 mm) of bottom ash, both the “true” fine fraction (resulting from the first screening) and the one obtained after grinding, are characterized by high variability.

Total aluminium partitioning in the fraction below 0.8 mm before grinding varies between 3.3% for cans and 20.5% for the mix of aluminium foils and of poly-laminated foils. This variability may be related to the characteristics of the packaging and the alloy, as well as to the operating conditions of the plant during the tests. More specifically, the highest contents of aluminium was found for the paper-laminated foil (18.6%) and the mix of foils (20.5%) and these results might be explained mainly by the structure of packaging. Compared to cans, the thickness and the technical strength of the foils are lower and lumps that form in the furnace are characterized by very small dimensions: this may facilitate their migration in the fine fraction of bottom ash.

Total aluminium partitioning in the fraction below 0.8 mm after grinding varies between 9.4% for cans and 51.1% for the mix of foils. The value related to cans is very low if compared to the others (28.7% the paper-laminated foils, 38.0% for trays and 51.1% the mix of aluminium foils and poly-laminated foils). For this type of packaging, total aluminium partitioning in the two fine fractions of bottom ash sums up to 12.7%: it follows that the loss of recoverable material is very small, as it is confirmed by the high amount of aluminium recovered as ingots. Similarly to what happens in the fine fraction before grinding, the high value found for foils is once again explicable by the structure of the packaging and the size of aluminium lumps.

Concerning the ingots from the melting process, there are many differences between the four types of packaging: about 81% of the aluminium in cans, 51% in trays, 47% in paper-laminated foils and 27% in the mix of foils was actually recovered from the bottom ash as ingots.

The relationship between aluminium packaging thickness and the recoverable amount of aluminium from the incineration residues is shown in Figure 4.4.

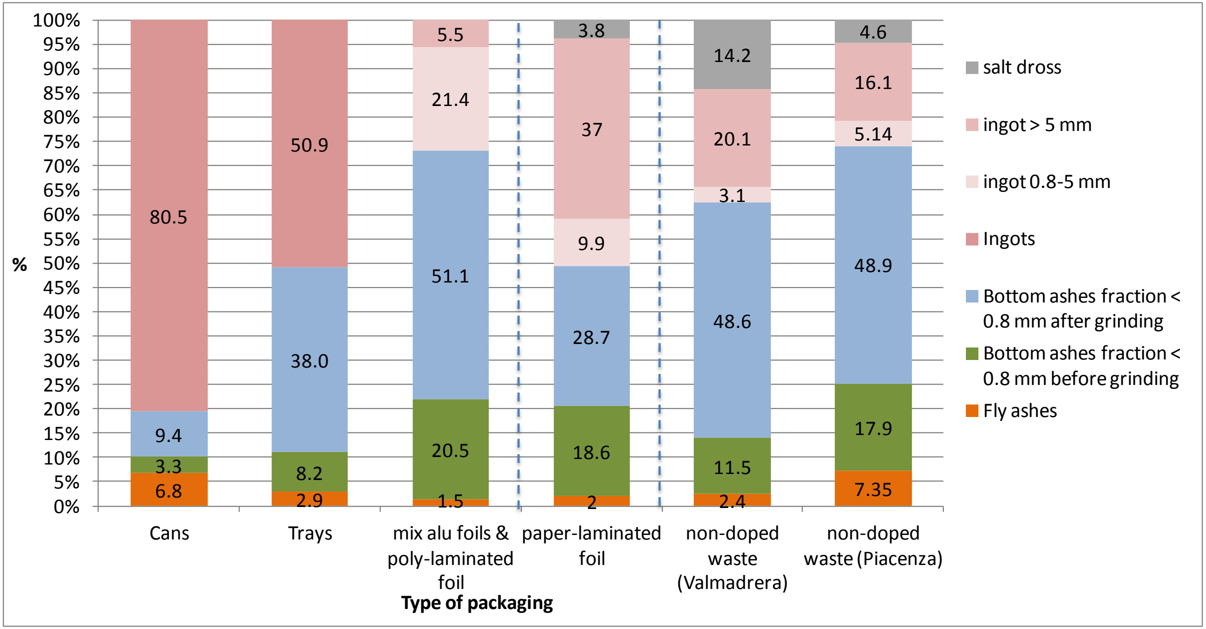


Figure 4.3. Partitioning of total Al in the residue of the incineration process for 4 different types of packaging material and for the mixed aluminium in the URW (non-doped sample). Cans, trays and the mix of aluminium foil and poly-laminated foil were tested in Valmadrera plant; the paper-laminated foil was tested in Piacenza. The salt dross was not included in the mass balance for the tests on cans, trays and the mix of foil and poly-laminated foil.

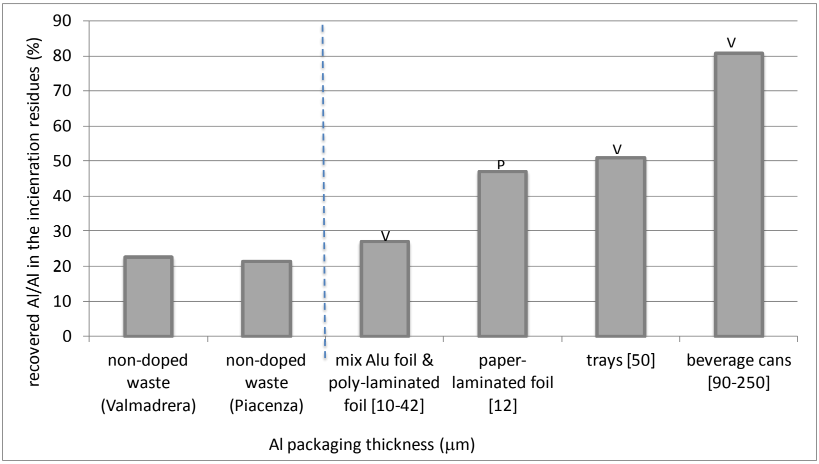


Figure 4.4. Relationship between aluminium packaging thickness and the recoverable amount of aluminium from the incineration residues. Cans, trays and the mix of aluminium foil and poly-laminated foil were tested in Valmadrera plant (V); the paper-laminated foil was tested in Piacenza plant (P).

The trend depicted in Figure 4.4 reveals that the recovery of aluminium from the incineration residues increases with the aluminium thickness in the tested packaging. Foils (Al thickness 10-42 μm) and trays (50 μm) are characterised by lower aluminium recovery yields if compared with beverage cans (90-250 μm), due to the formation of smaller lumps that are lost within the fine fractions.

For what concerns the foil, it is interesting to make a comparison between the paper-laminated foils tested in Piacenza and the mix of aluminium foils and poly-laminated foils tested in Valmadrera.

When poly-laminated foils are mixed with aluminium foil (Test #4), the amount of aluminium recoverable as an ingot decreases, against an increase of the aluminium in the fine fraction of the bottom ash, and 80% of the recovered aluminium results from the melting process of the 0.8-5 mm sub-fraction. The opposite can be observed when only poly-laminated foils[2] are fed to the furnace (test #7). In this case, 79% of the recovered aluminium comes from the >5 mm fraction and 21% from the 0.8-5 mm fraction, as reported in Figure 4.3.

These values suggest that the paper used in the paper-laminated foil improves the mechanical strength of the aluminium foil. In fact, during the combustion process, paper-laminated foil fragments in bigger pieces and creates lumps of bigger dimension compared to the pure aluminium foil.

Unfortunately, the test on the sole aluminium foil, carried out in Piacenza, did not turn out well and the results are not reported in Figure 4.3. The residence time of the waste during the test was significantly higher than the one theoretically expected. Consequently, the sampling did not cover the entire period during which the appearance of bottom ash representative of the doped waste took place. The evidence is provided by Figure 4.5 a) and b): only the initial growth phase of the curve was observed.

In any case, some considerations can be done based on the aluminium concentration observed in the residues of waste incineration. The behaviour of the two types of foils, the pure aluminium and the paper-laminated ones, resulted quite different. For the paper-laminated foil, a similar increase was observed for aluminium recovered as ingot and aluminium in the fine bottom ash fractions, as a consequence of the waste doping. For the aluminium foil, only the increase in the fine

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[2] Actually, only paper-laminated foils were used in test #7

fraction was observed, while aluminium recovery as ingot was not influenced at all (see Figure 4.5 c). This might be explained considering the different structure of the two types of foils, with the paper-laminated having a stronger structure that promotes a weaker fragmentation and thus a higher recovery as lumps. In addition, paper might have acted as a protective layer limiting aluminium oxidation.

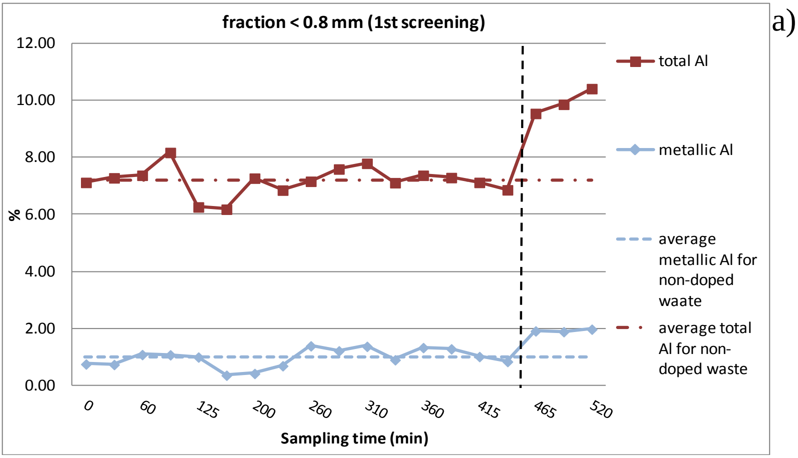

Figure 4.5. Test # 6 on aluminium foil. Trends of total and metallic aluminium percentage content (on the dry weight) in the two fine fractions below 0.8 mm and in the ingots. The vertical line indicates the beginning of the growth trend observed for these fractions

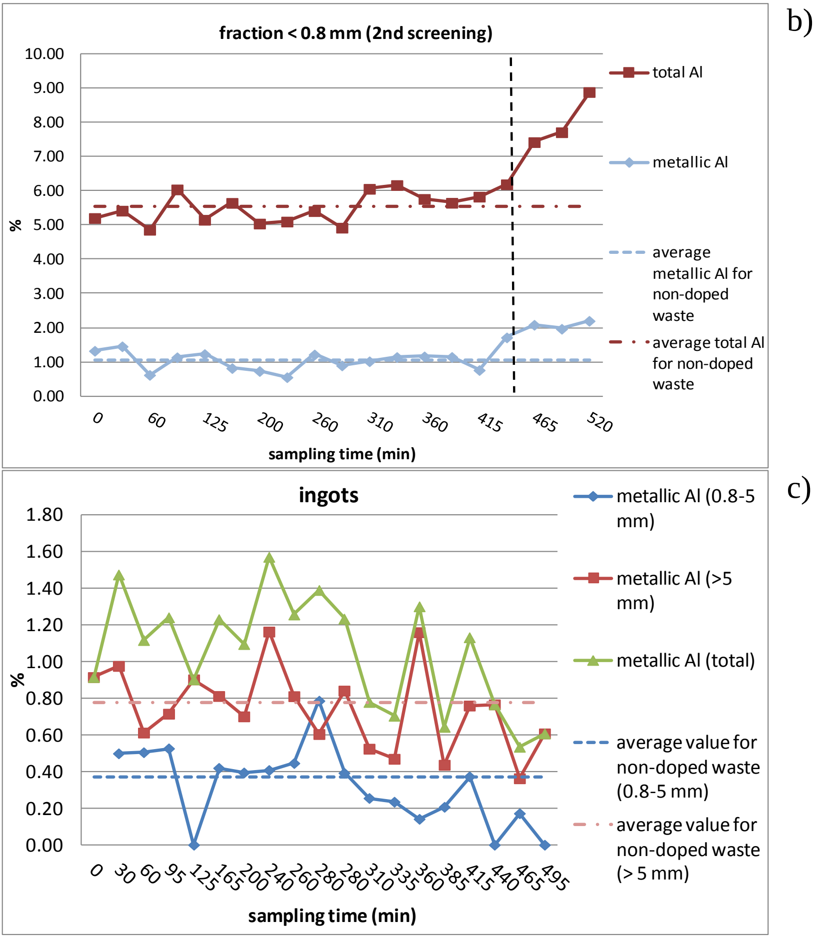

Figure 4.5. (follow) Test # 6 on aluminium foil. Trends of total and metallic aluminium percentage content (on the dry weight) in the two fine fractions below 0.8 mm and in the ingots. The vertical line indicates the beginning of the growth trend observed for these fractions.

As for the aluminium foil, figure 4.3. does not report the results of the two tests on spray cans, both the one carried out in Valmadrera and the one in Piacenza. In both the cases, in fact, the experimentation did not turn out well. Spray cans are characterised by thick walls and, during the combustion process, they create lumps of big dimension. When aluminium is present in small sized lump units, the loss of a lump or a fragment during the sampling does not significantly alter its average concentration. However, if lumps are big and limited in number, the loss of a single unit in the sampling phase substantially alters the results. During the test on spray cans in Valmadrera plant (test #3), sampling conditions of bottom ash were extremely harsh[3] and it is very likely that several lumps were lost during sampling operations, thus affecting the results of the analysis, as it is visible in Figure 4.6.

During the test on spray cans carried out in Piacenza (test #5), the sampling time was probably too short to see the effect of the waste doping and the percentage content of metallic aluminium in the ingots shows an irregular trend, apparently not linked to the doping of the waste, as represented in Figure 4.7. This implies that it was impossible to estimate the waste residence time and consequently the time interval for the numerical integration of the curve.

Despite the impossibility to evaluate the aluminium mass balance for the spray cans, an interesting consideration can be done on their behaviour in the furnace. Based on the aluminium concentration in the fly ash depicted in Figure 4.8, it is evident that spray cans do not influence the aluminium concentration in the fly ash. This can be explained by the structure of the spray cans, which are the thickest and more

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[3] A huge amount of vapours from the bottom ash pit prevented to have a clear view of the material during sampling operations.

robust among all tested packaging. The low specific surface and the mechanical properties promote the formation of big lumps with concentrate in bottom ash, whereas the fragmentation in little pieces that can leave the waste entrained by the flue gas is negligible.

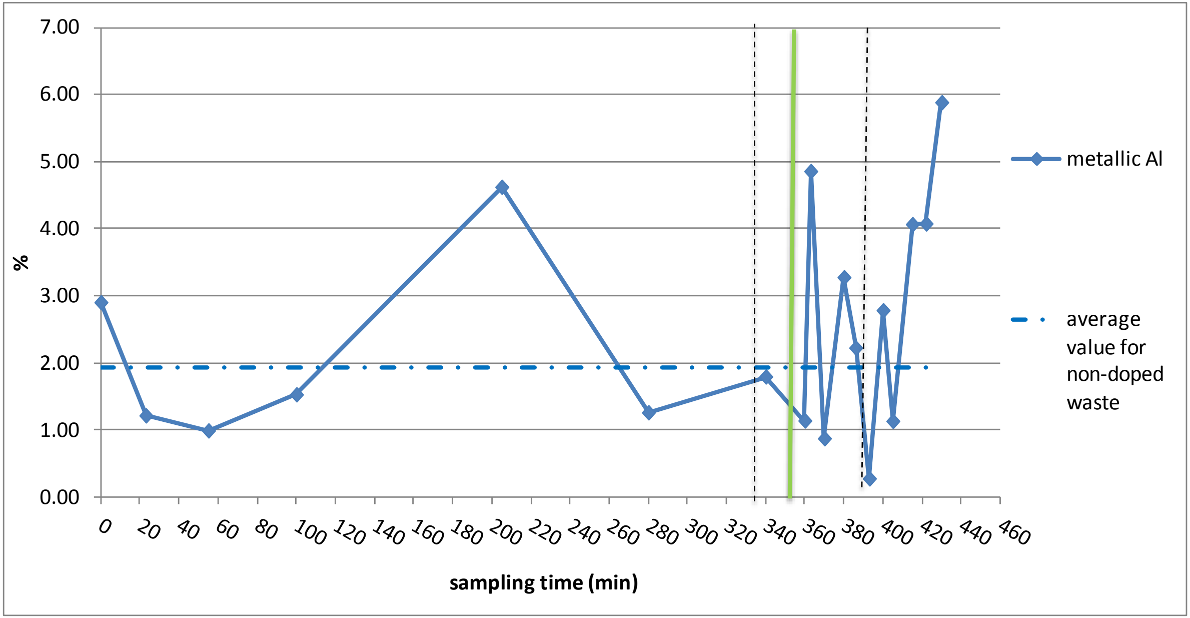

Figure 4.6. Test #3 on spray cans. Trend of metallic aluminium percentage content (on the dry weight) in the ingots resulting from the melting process. The bold vertical line indicates the beginning of the observed growth trend according to the analysis on total aluminium content in the fine fraction from the second screening.

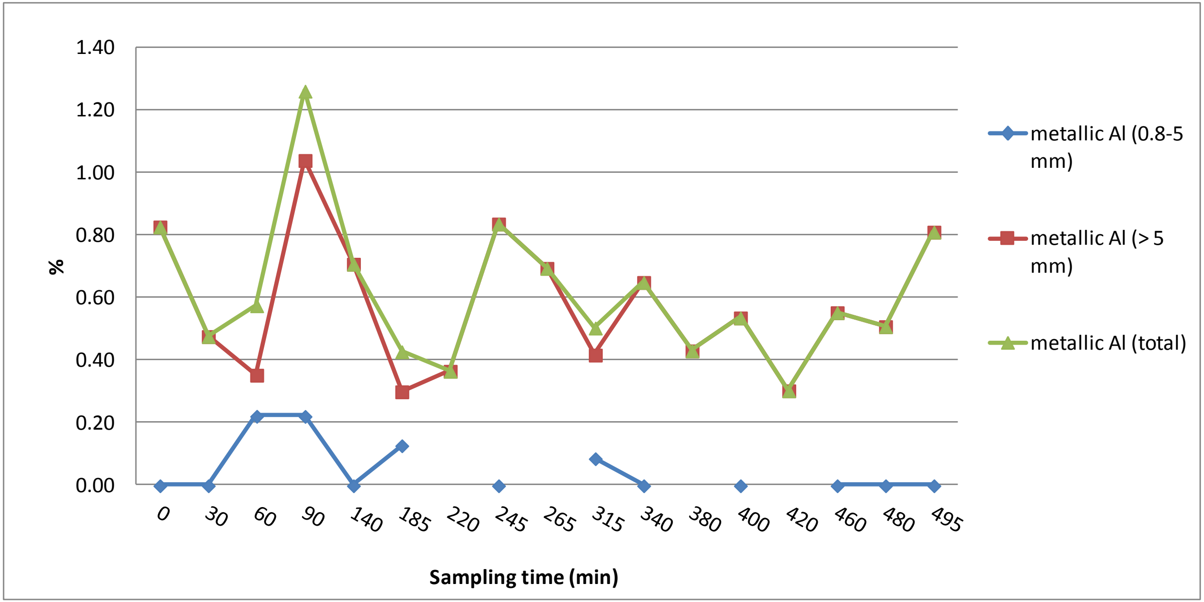

Figure 4.7. Test #5 on spray cans. Trend of metallic aluminium percentage content (on the dry weight) in the ingots resulting from the melting process of the 0.8 - 5 mm and > 5 mm sub-fractions. The null values for the 0.8-5 mm ingots stand for the samples from which it was not possible to extract the metal component during the melting process, whereas the missed values stand for the samples from which the ingot was recovered but it was too small to be analysed at the quantometer.

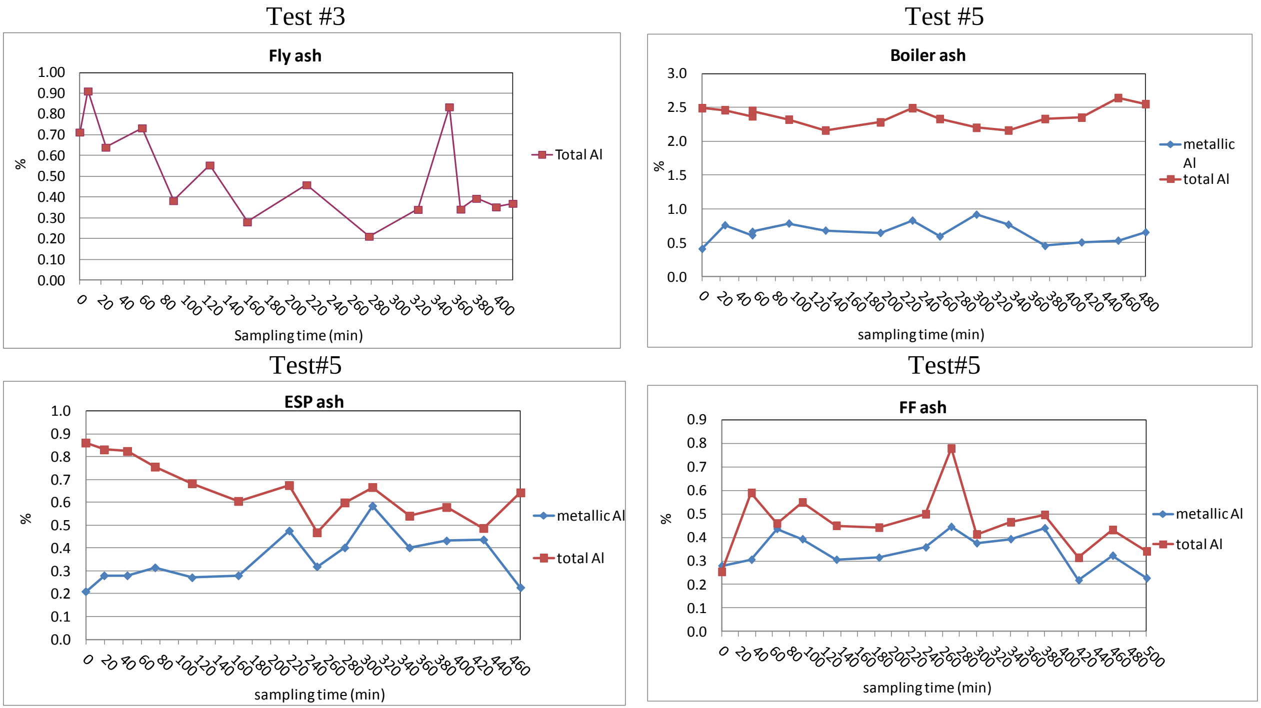

Figure 4.8. Tests #3 and #5 on spray cans. Percentage content of total and metallic aluminium measured in fly ash samples.

Aluminium oxidation

Values in Table 4.7 reports the percentage of aluminium in its metallic form for the tested packaging. Data about the non-doped waste will be discuss later.

Average values show the importance of the packaging thickness: the thicker the packaging is, the less it is oxidised during the combustion process. This is a consequence of the less surface area exposed to the oxidising gases. Of course thickness is not the only parameter influencing the behaviour of the packaging materials. The packaging technical strength plays an important role, avoiding the fragmentation of the material and the consequent increasing of the exposed surface.

As it is clear from Figure 4.9, the percentage of Al in the metallic form decreases when the poly-laminated foil is mixed with the aluminium foil, even if the thickness of the Al layer in the poly-laminated foil is lower than that of the pure aluminium foil. Paper acts as a protective layer, not only improving the mechanical strength of the packaging but also preventing Al oxidation.

These results call in question the CEN standard 1343 1:2004 that considers the Al foil < 50 μm recoverable in the form of energy, and thus completely oxidised. From our results, about 50% of the Al in the foils is present in the metallic form, despite the low thickness of these packaging materials. This suggests a revision of the standard, based on full-scale tests, in order to define new rules to account the Al fed to incineration furnaces for energy recovery or for material recovery.

Table 4.7. Metallic Al content in the incineration residues for the tested packaging and the non-doped waste (values expressed as percentage of metallic Al on total Al).

Residue	Non-doped waste (Valmadrera)	Non-doped waste (Piacenza)	Beverage cans (Test #1)	Trays (Test #2)	Mix aluminium foil and poly-laminated foil (Test #4)	Paper-laminated foil (Test #7)
Boiler ash	85.94	37.90	53	55	34.4	96.9
ESP ash		47.71				43.2
FF ash		76.74				76.7
Bottom ash fraction < 0.8 mm before grinding	26.58	12.02	4	96	5.6	19.6
Bottom ash fraction < 0.8 mm after grinding	24.76	17.91	70	63	24.8	4.9
Ingots 0.8 – 5 mm	100	100.00	100	100	100	100
Ingots > 5 mm		100.00			100	100
Dross salt	40.56	43.03	n.a.	n.a.	n.a.	43.6
AVERAGE	***46.17***	***37.43***	***90.8***	***82.6***	***41.2***	***54.8***

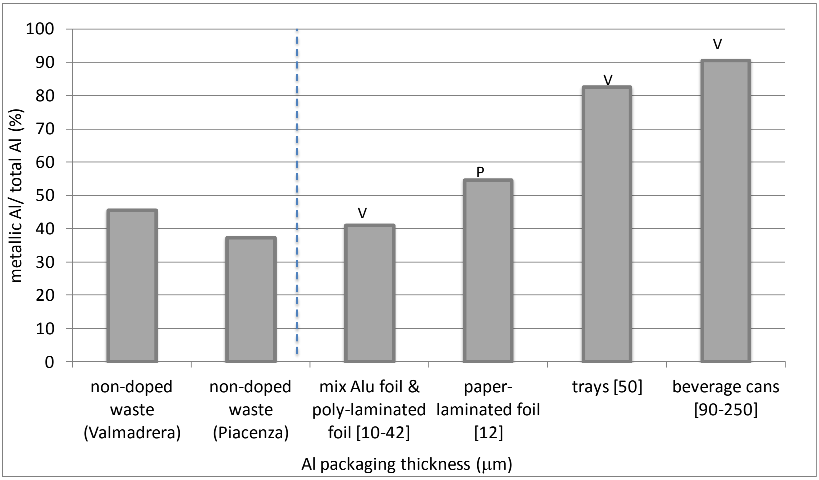

Figure 4.9. Relationship between aluminium packaging thickness and the percentage of aluminium in the metallic form in the incineration residues. Cans, trays and the mix of aluminium foil and poly-laminated foil were tested in Valmadrera plant (V); the paper-laminated foil was tested in Piacenza plant (P).

Considering each residue, the percentage of aluminium in the metallic form in fly ash does not show high variability between the different types of tested packaging. For cans, trays and paper-laminated foil, more than 50% of the aluminium is in the metallic form, with values that vary between 53% for cans to 68% for the paper-laminated foil. On the contrary, the aluminium in fly ash for the mix of foils and poly-laminated foil (test #4) is more oxidised, and only 34% is present in the metallic form.

The fine fractions of bottom ash are characterized by percentage of Al in the metallic form significantly different one from another. Concerning the fraction below 0.8 mm from the first screening, aluminium is entirely present in the oxidised forms for cans and foils (whose percentage of Al in the metallic form is equal to 4% for cans, 5.6% for the mix of foils and poly-laminated foils and 20% for the paper-laminated foil), whereas it is almost all in its metallic form for trays (96%). Concerning the fine fraction obtained from the second screening, the highest percentages of Al in the metallic form belong to cans and trays (70% and 63%, respectively), while foils are more oxidised (percentage of Al in the metallic form equal to 25% for the mix of foils and poly-laminated foils and 5% for the paper-laminated foils).

4.2.3. Non-doped waste

Aluminium flow rate

The aluminium partitioning in the residues of the incineration process was evaluated for the standard operating conditions of the two plants of Valmadrera and Piacenza. The results are reported in Figure 4.3.

The partition of aluminium in the residues of the combustion process results quite similar for the two plants. On average, about 61-67% of the aluminium concentrates in the fine fraction of the bottom ash and cannot be recovered with the current technologies. Only 21-23% can be thus recovered from the bottom ash and recycled as ingots. Out of this amount, 13-24% comes from the bottom ash fraction included between 0.8 and 5 mm and 76-87% from the fraction bigger than 5 mm. This means that, even if most of the aluminium scraps are recoverable through standard eddy current technologies, a non negligible amount can be recovered only in advanced treatment plant, equipped with a grinding stage and advanced eddy current separators.

The aluminium that during the combustion process concentrates in the fly ash results negligible and included between 2.5 and 7%.
For what concerns the data about the salt dross, it must be said that the melting process performed during the experimentation was characterized by a very low efficiency compared to the industrial process. In fact, the non-ferrous scraps recovered from the ash were melted together despite the high content of other-non ferrous metals. On the contrary, in the industrial processes, the non-ferrous scraps recovered from the bottom ash are diluted in a mix of pure Al scraps, achieving a better recycling efficiency. If we include the metallic Al lost in the salt dross during the melting process, the amount of Al potentially recoverable and recyclable from the ash thus increases up to 23-29%.

Comparing aluminium partitioning in the residues of the incineration process for the non-doped waste and for the selected packaging materials, we notice that the data of the URW are similar to that obtained for the foils. This seems to suggest that most of the aluminium in the URW consists of flexible packaging, like aluminium foil and poly-laminated foil. In fact, while the separated collection of cans and spray cans is well established and achieves a good efficiency, that of the flexible packaging is more complex. Most of this materials is in fact used during cooking and, being contaminated by food residues, is not collected at the source but thrown away in the URW. The recovery of these flexible packaging materials from the bottom ash is therefore very interesting and represents an important challenge, since it is complicated by the little dimension of the ingots that they form during the combustion process.

Aluminium oxidation and energy recovery
Less than 50% of the aluminium in the non-doped waste is present on average in the residues in the metallic form, as reported in Table 4.7. The plant design seems to have some influence on the observed data. Valmadrera plant, which is equipped with a forward-acting grate, shows a higher percentage of metallic Al compared to Piacenza plant, equipped with a backward-acting grate. Furthermore, the residence time of the waste on the grate and in the bottom ash extraction turned to be longer in Piacenza plant (9-10 hours in Piacenza plant and 4-6 hours in Valmadrea), which means that the aluminium scraps are exposed for a longer time to high temperature oxidation processes.

Even if most of the aluminium is presented in its oxidised form and thus cannot be recovered as material, it contributes to the energy developed during the combustion process. In fact, at combustion temperatures above 850°C, the complete oxidation of 1 kg Al into Al_2O_3 releases 31 MJ of energy, which corresponds to the same amount released by 1 kg of coal or 0.8 kg of fuel. The energy potentially recoverable from aluminium oxidation in the waste is reported in Table 4.8. It must be specified that all the oxidised aluminium has been assumed as Al_2O_3, thus resulting in a specific energy release equal to 31 MJ/kg. This is not necessarily true because aluminium in the 3+ oxidation state might be present in other mineral phases (such as ettringite, zeolites or other alumino-calcium hydrate compounds), resulting in different specific energy releases. Therefore, the results of the calculation must be considered as rough estimates.

On average, aluminium contribution to the energy released by the waste during the combustion process resulted equal to 1%, almost proportional to its presence in the waste.

Table 4.8. Potential for energy recovery from the oxidation of aluminium scraps in non-doped waste.

	Oxidised Al (kg /tURW)	**energy release from Al (MJ/tURW)**	**LHV waste (MJ/t)**	**Energy contribution of Al (%)**
non-doped waste (Valmadrera)	5.71	177.12	15391	1.15
non-doped waste (Piacenza)	4.62	143.25	14207	1.01

Other non-ferrous metals

Table 4.9 shows the average content of the principal elements in the ingots obtained from the melting process in the crucible for the non-doped waste. The results are reported separately for the tests carried out in Valmadrera plant (where all the non-ferrous metals were melted together) and in Piacenza plant (where the melting process was performed separately for the fraction < 5mm and > 5 mm).

As a general indication, the highest content of metals other than aluminium was found for Cu and Zn, in this order. On average the ingots recovered from Piacenza bottom ash are richer of other non-ferrous metals compared to those of Valmadrera plant.

For what concerns Piacenza plant, almost all the metal content in the ingots obtained from the melting of the 0.8 - 5 mm sub-fraction are significantly higher than the corresponding values for the sub-fraction above 5 mm. The reason mainly lies in the generally higher concentrations of heavy metals that concentrates in the bottom ash fraction below 2 mm, as reported by Hu et al., 2007 and also observed in chapter 5 of this thesis.

Table 4.9. Average contents of the principal elements in the ingots from the melting process for each type of tested packaging (non-doped waste).

	Cu (%)	**Zn (%)**	**Si (%)**	**Pb (%)**	**Mn (%)**	**Mg (%)**	**Fe (%)**	**Al (%)**
TEST ON VALMADRERA PLANT Total ingot								
Test #1								
AVERAGE	5.91	3.52	1.70	0.54	0.37	0.03	1.73	85.40
STD. DEV.	2.83	1.72	1.28	0.26	0.12	0.01	0.56	3.94
Test #2								
AVERAGE	5.18	3.10	1.31	0.45	0.45	0.03	1.23	87.80
STD. DEV.	5.03	1.55	0.66	0.18	0.11	0.01	0.30	5.95
Test #3								
AVERAGE	6.87	3.09	1.53	0.73	0.36	0.03	1.28	85.73
STD. DEV.	4.70	1.18	0.86	0.22	0.09	0.01	0.27	5.33
Test #4								
AVERAGE	2.56	0.91	1.99	0.09	0.35	0.08	1.27	91.96
STD. DEV.	0.75	0.42	0.57	0.08	0.14	0.08	0.11	4.36
TOTAL AVERAGE	*5.13*	*2.66*	*1.63*	*0.45*	*0.38*	*0.04*	*1.38*	*87.72*
TOTAL STD. DEV.	*4.08*	*1.56*	*0.92*	*0.27*	*0.11*	*0.03*	*0.43*	*5.21*
TEST ON PIACENZA PLANT								
Ingot (0.8- 5 mm)								
Test #5								
AVERAGE	8.58	5.15	5.45	0.32	0.74	0.11	4.14	72.78
STD. DEV.	6.14	3.38	8.48	0.27	0.66	0.18	4.74	12.73
Test #6								
AVERAGE	11.97	6.24	1.08	0.67	0.50	0.02	1.82	76.66
STD. DEV.	3.82	1.71	0.33	0.40	0.10	0.01	0.88	5.92
Test #7								
AVERAGE	17.78	6.78	0.96	0.65	0.47	0.02	2.49	67.47
STD. DEV.	1.72	1.34	0.04	0.21	0.01	0.01	0.51	3.21
TOTAL AVERAGE	*11.88*	*6.08*	*1.90*	*0.58*	*0.54*	*0.04*	*2.32*	*73.59*
TOTAL STD. DEV.	*4.66*	*2.02*	*3.74*	*0.37*	*0.29*	*0.08*	*2.19*	*7.60*

Table 4.9. (follow) Average contents of the principal non-ferrous metals and of the iron in the ingots from the melting process for each type of tested packaging (non-doped waste).

TEST ON PIACENZA PLANT								
	Cu (%)	**Zn (%)**	**Si (%)**	**Pb (%)**	**Mn (%)**	**Mg (%)**	**Fe (%)**	**Al (%)**
Ingot (>5 mm)								
Test #5								
AVERAGE	4.47	3.46	1.36	0.31	0.35	0.03	0.79	86.50
STD. DEV.	4.42	3.36	1.15	0.23	0.24	0.03	0.47	8.98
Test #6								
AVERAGE	5.01	5.33	1.50	0.56	0.27	0.07	0.76	85.03
STD. DEV.	3.14	4.14	1.52	0.32	0.06	0.06	0.36	6.63
Test #7								
AVERAGE	1.48	6.02	1.06	0.13	0.33	0.03	0.63	82.75
STD. DEV.	1.17	4.19	0.81	0.06	0.05	0.00	0.09	5.02
TOTAL AVERAGE	*4.54*	*4.46*	*1.41*	*0.42*	*0.31*	*0.05*	*0.77*	*85.14*
TOTAL STD. DEV.	*3.77*	*3.79*	*1.29*	*0.30*	*0.17*	*0.05*	*0.40*	*7.38*

5. RECOVERY OF ALUMINIUM FROM THE BOTTOM ASH FINE FRACTION

According to the results reported in Chapter 4, about 21-23% of the aluminium present in the URW in Northern Italy can be actually recovered from the bottom ash and recycled. This amount is probably underestimated due to the low efficiency of the melting process performed during the experiment tests. If we consider all the metallic Al potentially recoverable from the ash (including the metallic Al lost in the salt dross during the melting process), the value increases up to 23-29%.

Out of this amount, 13-24% comes from the bottom ash fraction smaller than 5 mm, whose recovery is not efficient in bottom ash treatment plant equipped only with standard eddy current machines and without a grinding stage. In fact, the recovery rate of ECS drops from almost 100% for particles larger than 20 mm to virtually zero for particle size between 5 and 12 mm, depending on the number of screening steps and on the plant layout and complexity (Berkhout et al., 2011).

This chapter analyses two different treatment options for the fine fraction (< 4 mm) of MSWI bottom ash: a) recovering metallic Al through an advanced treatment process including additional steps of grinding and sieving; b) producing hydrogen gas by reacting metallic Al with water under alkaline anaerobic conditions.

5.1. MATERIALS AND METHODS

Sampling procedure

The research was partially carried out in Sweden, at Lund University, and partially in Italy.

The bottom ash was sampled in a bottom ash treatment plant located in South Sweden, with a total capacity of about 40,000 tonnes per year. Bottom ash is produced at a nearby MSW incineration plant treating residual waste in a grate furnace with wet extraction system. The treatment process is quite complex, as illustrated in Figure 5.1, including a number of sorting steps with several magnets and ECS for the specific particle sizes. The study focuses on the particles smaller than 4 mm from which non-ferrous scraps are separated by means of a standard ECS. Bottom ash was sampled from the conveyor belt both upstream and downstream of the ECS separator.

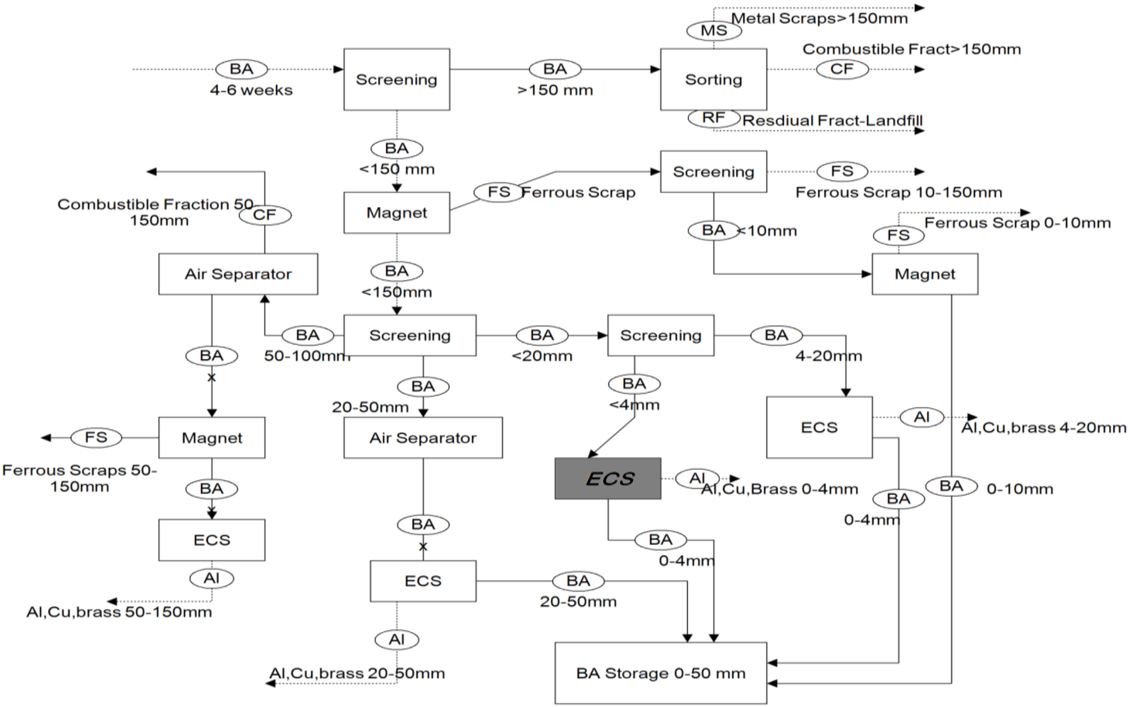

Figure 5.1. Layout of the bottom ash treatment plant. The ECS highlighted in grey is where sampling took place.

Evaluation of the aluminium concentration in the bottom ash

In the laboratory, four subsamples of about 5 kg each were obtained after a quartering procedure. The two upstream samples of bottom ash were labelled U1 and U2, and the two downstream samples D1 and D2.

The samples U1 and D1 were properly treated according to the procedure illustrated in Figure 5.2. As for the tests described in Chapter 4, the pre-treatments were designed to simulate an advanced process for the recovery of aluminium, including a grinding and a sieving stage, as well as to facilitate their subsequent laboratory analysis. They were crushed manually in a mortar to promote metals liberation and then they were sieved with 1 mm mesh. In this way, it was possible to isolate the coarse fraction (above 1 mm) enriched of metals, which unlike the inert material are not crushed but just flattened during the crushing stage. The fractions smaller than 1 mm after crushing were labelled U1.0-1 (upstream) and D1.0-1 (downstream), respectively. These samples represent the fractions whose aluminium content cannot be recovered with current ECS technologies. In addition, Al particles smaller than 1 mm are usually not recycled. In fact, the current technologies used in the smelter for secondary aluminium production allow to recycle only the Al particles bigger than 0.8-1 mm. Particles < 1 mm are fully oxidised in the smelter, reducing the efficiency of the recycling process.

The fractions bigger than 1 mm after crushing were labelled as U1.1-4 and D1.1-4. Ferrous metals were removed from the two samples by using a magnet and were then discharged. Sample U1.1-4 represents the non-ferrous lumps potentially recoverable through an advanced bottom ash treatment process including a crushing step (i.e. the process reproduced during the samples treatment and illustrated in Figure 5.2). Sample

D1.1-4 represents the lumps that cannot be recovered by the standard ECS present in the plant depicted in Figure 5.1.

The metallic aluminium concentration in the samples U1.0-1 and D1.0-1 was measured using the soda attack method, previously illustrated in Chapter 4. The instrument used for the evaluation is depicted in Figure 5.3. A 5 g ash sample was introduced in the bottle flask. After creating the vacuum in the instrument, the valve of the dropping funnel filled with 100 ml of sodium hydroxide (NaOH 40%) was opened. The flask was heated with an electrical resistance in order to accelerate the reaction and improve the mixing of the material with the help of the convective movements. The difference between the initial and the final pressure measured by means of a digital sensor for gas velocity and flow meter measurement (Flowtest ST by Tecora) was related to the gas produced by 1 g of pure aluminium, used for the instrument calibration. Four replicates were carried out for each sample. The total aluminium content in the same samples (U1.0-1 and D1.0-1) was evaluated by means of X-ray fluorescence spectroscopy (XRF).

Samples U1.1-4 and D1.1-4 were melted with salt (70% NaCl and 30% KCl) in a crucible, with the same procedure described in Chapter 4, and the salt dross was analysed with the same procedure as for the samples U1.0-1 and D1.0-1. The recoverable metal ingot was finally analysed for its content of Al (all considered metallic) and other non-ferrous metals by an optic emission spectrometer (OES).

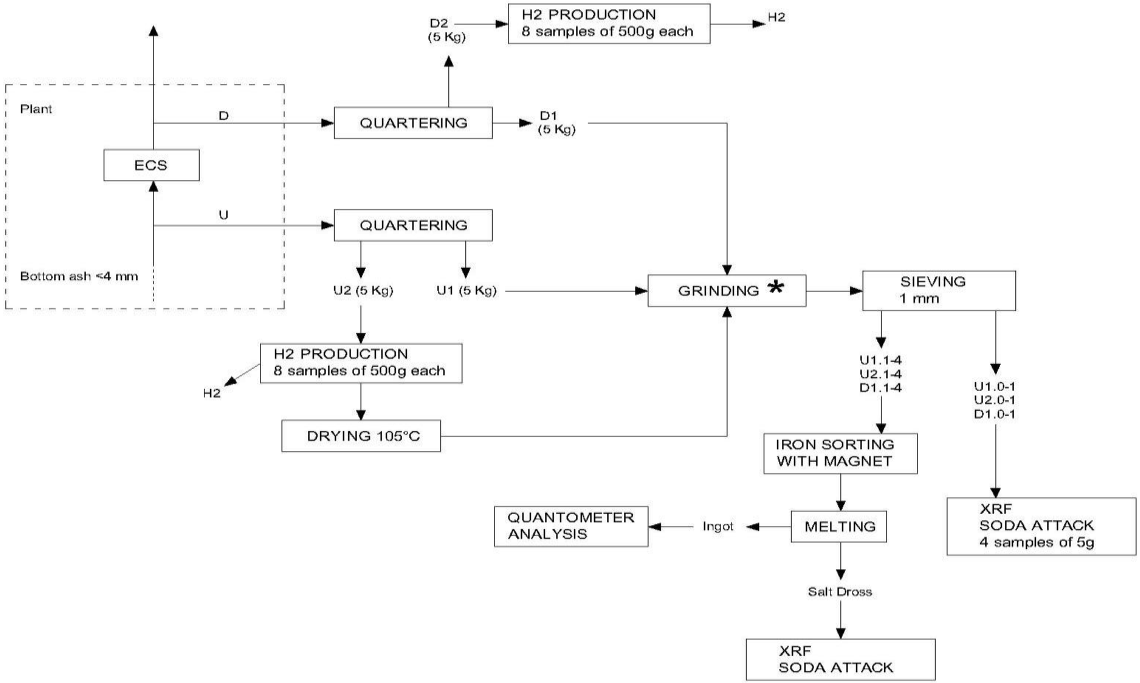

Figure 5.2. Sampling and analysis procedures adopted for the bottom ash. (*) From this point onwards, the procedure is identical for the three samples.

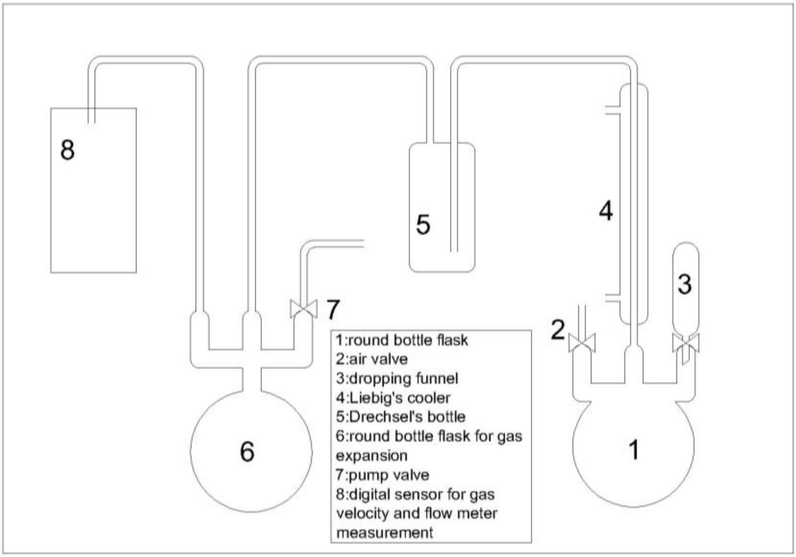

Figure 5.3. Laboratory device used to evaluate the concentration of metallic Al in the bottom ash with the soda attack method.

H_2 recovery experiments

Samples U2 and D2 were used to simulate a process for H_2 recovery from the bottom ash. Eight uncrushed samples (500 g each) were put in 5 l glass bottles and mixed with NaOH at 10M at L/S of 1. The produced gas was recovered in gas begs and then extracted and measured with the help of a 100 ml syringe at the end of the experiment. The whole setup was run at room temperature for 48 hours with sporadic mixing to increase the contact between the solid and the liquid phase. The procedure aims to simulate a simple process where H_2 is recovered from the bottom ash that is stored at ambient temperature. Alkali was used as promoter for the reaction to proceed rapidly. The results from the two samples, U2 and D2, were compared to check whether aluminium removal with a standard ECS significantly affects H_2 production, as one might expect.

After the gas recovery, sample U2 was dried in an oven at 105°C for 24 h and analyzed with the same procedure as for the sample U1. This allowed to evaluate if the H_2 produced by the bottom ash mainly comes from the lumps or from the particles in the fine fraction. The loss of aluminium potentially recoverable with ECS technologies, due to the oxidation of the lumps during the soda attack process, was also evaluated.

Sample D2 was non analysed after H_2 production, because its aluminium content after gas recovery was considered of poor interest.

5.2. RESULTS

5.2.1. Aluminium recovery

Table 5.1 reports the total and metallic aluminium content of the sampled bottom ash. As explained in Chapter 4, the ingot fraction is representative of the metal actually recoverable from the bottom ash. Since it is obtained from the melting process, the numerical value is representative of the efficiency of the whole recycling process. On the contrary, the aluminium in the bottom ash fraction < 1mm represents a loss, because it cannot be recovered from bottom ash, neither recycled in the secondary aluminium smelter. The table also provides aluminium concentration in the salt dross produced during the melting process, which includes Al in the oxidized form as well as the metallic Al trapped in the salt. In this section, only the results from samples U1 and D1 are discussed. The results of the other upstream sample U2 will be commented in the next session.

Table 5.1. Al concentration in the bottom ash fraction < 4 mm upstream (U1 and U2) and downstream (D1) of the ECS. Sample U2 represents the bottom ash after H_2 recovery.

Sample Name		Description	Total Al (%w/w dry BA)	Metallic Al (%w/w dry BA)	Metallic Al/Total Al (%)
U1	U1.0-1	BA < 1 mm	7.53 ± 0.04	0.93 ± 0.13	12.34
	U1.1-4	BA 1-4mm ingot	0.26 ± 0.00	0.26 ± 0.00	100.00
		BA 1-4 mm salt dross	0.43 ± 0.00	0.07 ± 0.00	16.08
	Total		**8.22 ± 0.04**	**1.26 ± 0.13**	**15.28**
D1	D1.0-1	BA < 1 mm	7.33 ± 0.18	0.53 ± 0.07	7.19
	D1.1-4	BA 1-4 mm ingot	0.17 ± 0.00	0.17 ± 0.00	100.00
		BA 1-4 mm salt dross	0.19 ± 0.00	0.02 ± 0.00	12.70
	Total		**7.69 ± 0.18**	**0.73 ± 0.07**	**9.43**
U2	U2.0-1	BA < 1 mm	7.92 ± 0.26	0.27 ± 0.02	3.37
	U2.1-4	BA 1-4 mm ingot	0.03 ± 0.00	0.03 ± 0.00	100
		BA 1-4 mm salt dross	0.49 ± 0.00	0.10 ± 0.01	20.95
	Total		**8.44 ± 0.26**	**0.40 ± 0.03**	**4.71**

Total average Al concentration in the 0-4 mm fraction of the bottom ash is 8.2% in the sample collected upstream the ECS (sample U1) and 7.7% in the sample collected downstream the ECS (sample D1). The similar aluminium content in the two samples shows the modest efficiency of the ECS when applied to a fine particles stream.

More than 90% of the total Al is found in the fraction < 1 mm (7.5% out of 8.2% in sample U1 and 7.3% out of 7.7% in sample D1). Therefore, it cannot be separated from the bottom ash stream with the current ECS technologies. Most of the Al in the bottom ash below 5-6 mm comes, in fact, from the light packaging and the Al foils, as showed in Chapter 4 and reported by Hu et al. (2011). These materials are usually characterised by a low thickness and mechanical strength, which facilitate their concentration in the fine fraction of the ash as well as their high oxidation level.

During combustion, the aluminium scraps undergo oxidation processes which affects the amount of metallic Al in the lumps separated from the bottom ash stream through ECS. These processes are particularly important for the small scraps which concentrate in the fine fraction of the bottom ash, whose small size and the consequent high specific surface can easily explain their high oxidation level. In fact, only less that 15% of the Al in the analysed samples is present in the metallic form and, thus, can be potentially recycled.

These two aspects, the high content of Al in the bottom ash fraction below 1 mm and the high oxidation level, determine the modest recovery of Al detected in the analysed bottom ash samples.

In more detail, focusing on the metallic Al, its concentration in the upstream sample U1 is equal to 1.26% of the weight of dry bottom ash. If we consider only the Al potentially recoverable, i.e. that in the bottom ash fraction above 1 mm, the percentage decreases to 0.33% of the weight of dry ash. However, during the recycling process part of this Al is unavoidably trapped in the salt dross. The percentage of Al actually recoverable as an ingot is thus lower and equal to 0.26% of the weight of dry ash. This means that only 21% of the metallic Al in the ash can be actually recovered as an ingot, which corresponds to 3.1% of the total Al in the bottom ash.

After the ECS (sample D1), the total content of metallic Al decreases to 0.73% of the dry weight of the bottom ash and, if we consider only the Al actually recoverable as an ingot, the figure decreases to 0.17% of the dry weight of the ash (0.2% if we neglect the recycling process, including the amount of metallic Al in the salt dross).

The difference between the recovered ingot from the bottom ash samples upstream and downstream the ECS (samples U1 and D1, respectively) represents the amount of Al lumps separated by the ECS operating in the investigated plant and then recycled. This is representative of a standard bottom ash treatment plant based on a single ECS and without a grinding stage aimed at liberating the metal particles. On the contrary, the aluminium recovered from the sample U1 is representative of the efficiency of an advanced bottom ash treatment process, including a grinding stage.

A standard bottom ash treatment plant can, thus, recover only 32% of the aluminium potentially recoverable with an advanced process, as resulting from Eq. 5.1, which also includes the efficiency of the recycling process.

$$\eta_{\text{standard BA treatment plant \& melting process}} = (\text{ingot.U1} - \text{ingot.D1})/\text{ingot.U1} \qquad \text{(Eq. 5.1)}$$

where the prefix *ingot.* is the concentration of the aluminium recovered as an ingot in the bottom ash samples U1 and D1 and referred to the weight of the dry bottom ash, as reported in Table 5.1.

Since the non-ferrous metals recovered from the bottom ash were melted together during the tests, without a previous separation of the Al lumps from the other non-ferrous metals like in full-scale smelters, a non-negligible amount of metallic

Al was lost in the salt dross. If we assume a recycling efficiency of 100%, including the fraction of metallic Al trapped in the salt dross, only 47% of the Al lumps actually recoverable through an advanced treatment process of the bottom ash can be recovered in a standard plant (Eq. 5.2). This underlines the importance of using advanced ECS technologies combined with subsequent crushing steps for liberating the non ferrous metal lumps from the ash.

$$\eta_{\text{standard BA treatment plant}} = [(\text{ingot.U1}+\text{salt dross.U1}) - (\text{ingot.D1}+\text{salt dross.D1})] / (\text{ingot.U1}+\text{salt dross.U1}) \quad \text{(Eq. 5.2)}$$

where *salt dross.* represents the amount of metallic Al trapped in the salt dross of the samples U1 or D1, expressed on the dry weight of the bottom ash.

Characteristics of the non-ferrous lumps

Non-ferrous lumps separated during the samples pre-treatment and subsequently melted were analysed to evaluate their composition (Table 5.2). For samples U1 and D1, Al concentration is between 25 and 30%, much lower than what reported in the literature for the non-ferrous lumps extracted by the whole bottom ash, where Al is usually around 60%, and those observed in Chapter 4. On the contrary, surprisingly high concentration of Cu (between 50 and 60%) and Zn (about 6.5%) was measured. Ferrous contamination probably due to the stainless steel not separated during the pre-treatment process is also not negligible. The same can be said for precious and rare metals such as silver and vanadium, whose concentration in the ingot corresponds to about 0.7-1.8 g of Ag per kg of dry bottom ash and 0.9-1.5 g of V per kg of dry bottom ash.

The lumps recoverable from the 0-4 mm bottom ash fraction are richer in other non-ferrous metals compared to those separated by the coarse bottom ash. According to Hu et al. (2007), Al lumps usually concentrate in the bottom ash fraction above 6 mm, while Cu, Zn and Pb scraps concentrate in the fraction smaller than 2 mm. These metals, in fact, mainly come from the electronic equipments incorrectly routed in the residual MSW and they are characterized by a very small size compared to the Al packaging and items.

The composition of the lumps upstream and downstream the ECS (i.e. samples U1 an d D1) is quite similar, meaning that the ECS operating in the plant has a similar recovery efficiency for all the non-ferrous metal lumps.

Table 5.2. Average composition (% w/w) of the ingots formed by melting of metal lumps recovered from the bottom ash sampled upstream (sample U1) and downstream (sample D1) the ECS.

Sample	Al	Cu	Zn	Fe	Pb	Cr	Ni	Sn	V	Ag
U1	24.46	60.81	6.20	2.95	1.67	0.16	0.51	0.72	0.14	0.18
D1	29.74	51.90	6.97	2.68	4.21	0.12	0.34	1.67	0.15	0.12
U2	6.21	69.42	11.95	2.15	6.65	0.05	0.54	0.77	0.18	0.07

5.2.2. H_2 production from the bottom ash

Table 5.3 presents the amount of H_2 produced by the bottom ash samples, which resulted nearly 11 l/kg of dry ash for the upstream sample U2 and 6 l/ kg of dry ash for the downstream sample D2.

We can observe that the amount of H_2 recoverable from the ash is nearly halved after the ECS. This decrease is not surprising, since ECS removes the aluminium lumps which in our case contributed for 23% of the H_2 released by the ash (Table 5.3).

The rest of the decrease can be explained by the oxidation of Al. Soler et al. (2009) and Ilyas et al. (2010) reported that the formation of an oxide layer prevents Al from reacting with water for hydrogen production. In some situations, this oxide layer may not lead to H_2 production even when corroded with alkali. Zhang et al. (2009) have reported that in alkaline solution, oxide coatings can dissolve into the following species: Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)^{-4}$.

In terms of Al utilisation, H_2 production from the bottom ash is really interesting and performs much better than the mechanical separation process. In fact, about 71% of the metallic Al in the fraction smaller than 1 mm and about 60% in the lumps is converted by reaction with water. According to the data reported in Table 5.1, after H_2 recovery the amount of metallic Al in the < 1mm bottom ash fraction decreases drastically from 0.93% to 0.27% of the dry bottom ash weight (samples U1 and U2, respectively) and the one in the recoverable fraction (i.e. metallic Al in the bottom ash fraction > 1 mm including the salt dross) decreases from 0.33% to 0.13% of the dry bottom ash weight, for the same total Al concentration. This allows to use also the aluminium particles < 1mm (as evident from table 5.3), that represent a loss of material in traditional bottom ash treatment plants.

As a matter of fact, all the metallic Al that reacts with soda is converted into its oxidised form, which means that it cannot be recycled anymore. It is, therefore, evident that the recovery of aluminium scraps and the production of H_2, are incompatible. In fact, an eventual recovery of the non-ferrous scraps downstream of the bottom ash treatment for H_2 production will have a very low efficiency. At the same time, performing H_2 recovery on the bottom ash downstream of the ECS means to recover less gas, because most of the lumps have already been removed by the ECS.

It is interesting to notice that the ingot composition varies after H_2 recovery, with a further reduction of the already low Al concentration (Table 5.2).

Table 5.3. H_2 production (l kg^{-1} of dry bottom ash at 0°C and atmospheric pressure) from the bottom ash sampled upstream (sample U2) and downstream (sample D2) the ECS, evaluated following the procedure illustrated in paragraph 5.1.

Sample	Average		Std.Dev	p-value t-test
U2	10.8	(77% from BA< 1mm) (23% from BA > 1mm)	4.9	0.0029
D2	5.7		1.2	

5.2.3. Economic and environmental considerations

Before a new system is developed, the economic feasibility of improving aluminium recovery from the fine fraction of the bottom ash by substituting a standard ECS with an advanced one, or by developing H_2 recovery, must be evaluated by comparing the amount and the value of the recovered aluminium lumps or H_2 with the cost of the plant.

To evaluate the additional cost of an advanced bottom ash treatment plant compared to a standard one, the economic data from Kohaupt (2011) were used. The cost of a standard ECS is assumed to be 85,000 Euros, whereas that of an advanced ECS, for example one at high frequency, is assumed equal to 130,000 Euros for the same capacity. Considering also a grinding machine to improve metals recovery and a screen, which cost about 500,000 Euros and 200,000 Euros respectively, the total investment amounts to 745,000 Euros. The installed power of the same machines is assumed equal to about 12 kW for the advanced ECS, 10 kW for the standard one, 50 kW for the grinding machine and 20 kW for the screen. Considering that the plant operates 2400 h/y, this leads to an increased energy consumption of 172 MWh/y, which corresponds to 35,700 Euros/y (assuming that the electricity price is equal to about 0.0784 Euro/kWh for industrial customers in Sweden as reported by the Europe's energy portal). Assuming yearly maintenance costs equal to 10% of the total investment and an interest rate of 2.5% with a description period of 5 years, the bottom ash treatment costs would increase by 2 Euros/t compared to the standard situation. However, thanks to the installation of an advanced ECS and a grinding stage, aluminium lumps recovery increases by about 200%. Moreover, other non-ferrous metals are recovered with the Al lumps. Considering the average ingot composition reported in Table 5.2 and a market price of 800 Euros/t for the whole non-ferrous lumps, the earning increases to 3.9 Euros per ton of bottom ash. Thus the direct advantage of improving metal recovery from the bottom ash amounts to nearly 2 Euros per ton of treated bottom ash.

From an environmental point of view, it is clear that the improvement of the recovery efficiency of Al would mean that less metals are left inside the ash which could undergo transformation and release gas during bottom ash reuse. Moreover, recycling of metals means a huge emission saving compared to the virgin production, as reported by Grosso et al. 2010 and Giugliano et al., 2011.

For what concerns H_2 production, the economic evaluation is more difficult, because it is still a laboratory-scale process and it needs further evaluations with different ash fractions at bench and pilot scale. The costs are related to the construction of a reactor for the treatment of the bottom ash with a system for H_2 collection, the use of soda and the electricity consumption. A further aspect to be considered is the safety concerns in H_2 storage and utilisation.

Independently on the actual investment, even if H_2 production is very interesting in terms of Al utilisation, as illustrated in Chapter 5.2.2., it would not be cost effective in the present case study. In fact, the production of gas is related only to the metallic Al content in the ash which, in the specific case, was quite low in the 0-4 mm ash fraction, thus leading to a modest H_2 production. In addition, we must consider that the lower heating value of H_2 at atmospheric pressure is very modest. Assuming that the produced H_2 is directly utilized at the waste incineration plant where bottom ash is produced, as a fuel in the furnace, its contribution to the total energy released by the waste + H_2 combustion would be, in fact, negligible (Table 5.4), too modest to lead to any influence on the incinerator thermal cycle and to justify any investment.

Table 5.4. Estimate of H_2 production in a MSW incinerator plant and of is contribution to the total thermal load.

	MSW		**H_2**	
LHV	kJ/kg	15,000	kJ/m_n^3	10,900
production	t/y	200,000	m_n^3/y	427,068*
Energy contribution	%	99.85	%	0.15

*Evaluated considering:
H_2 production= 10.8 l kg^{-1} of dry BA at 0°C and 1 atm
BA= 20% of the MSW weight
BA moisture= 10.5%.

In terms of ash quality, on the contrary, promoting H_2 production plays a positive role, facilitating its reuse as a construction material without further problems of swelling and expansion. Furthermore, the production of hydrogen gas converts most of the metallic Al into its hydroxide form which, if precipitated, could act as a binder for metals as well as the ash itself. However, upon drying the ash shows cementatious behaviour due to formation hydroxides, which could be negative, because formation of Al-hydroxide gel can lower the aggregate stability. Therefore mechanical strength of aggregates after the carbonation and drying needs to be tested.

Based on the above considerations, in this specific case study aluminium recovery should be preferred to H_2 production. At this initial stage of research, it is however not possible to extend such findings to other situations. The choice of a particular process should consider the specific context and balance the presumed benefits against financial and environmental costs. According to the actual bottom ash composition and to the Al distribution into the different particles fractions, H_2 production might turn to be more advantageous than Al recovery. For example, when most of the scraps consists of other non ferrous metals, such as Cu, Zn and eventually rare and precious metals, the reduction of the amount of recoverable metallic Al as a consequence of H_2 recovery could be economically advantageous, provided that the ECS is opportunely designed to maximize the recovery of other non-ferrous metals instead of aluminium lumps.

In any case, further experimentation would be required, including the investigation of the leaching behaviour of the elements after H_2 production and the evaluation of the environmental impacts of the two processes. Moreover, a comparative life cycle assessment would provide much better understanding of the benefits of the two processes.

6. CONCLUSIONS

Recovering aluminium and other non-ferrous metals from waste incineration bottom ash has become a common practice in the last decades. The concentration of these metals in the bottom ash can be higher than that in the ore, making their recovery advantageous from an economical point of view. In addition, significant environmental benefits are associated to their recycling, and their separation is crucial in view of the recovery of the inert fraction of bottom ash.

Despite metals recovery is a common practice, the correct design of the plant is a hard task, since it requires to know how much aluminium is in the ash and what are its main characteristics, in terms of dimensional classification of the lumps and of their quality, expressed by the oxidation level and the presence of other non-ferrous metals.

All these aspects make easily understandable why metal recovery from the ash is one of the hot topic of waste management.

The efficiency of metal recovery from the bottom ash is very uncertain. Despite the huge number of publications about this topic, finding an average value suitable for all Europe is rather impossible. The separated collection varies from one country to another, thus influencing the amount of aluminium in the waste and its composition. Aluminium can, in fact, be present in the waste as packaging or as other materials (like pots etc). Among the packaging materials, we can find cans, spray cans, foils etc, whose recovery from the ash is very different, as resulted from the tests reported in the thesis.

The recovery of the aluminium packaging from the ash and its oxidation level in the residues of the incineration process is strictly related to the structure and the mechanical properties of the material. About 81% of the aluminium in the cans can be recovered from the bottom ash and recycled as secondary aluminium, but this amount decreases to 51% when trays are considered, 27% for a mix of aluminium and poly-laminated foils and 47% for paper-laminated foils. The recovery of aluminium from the incineration residues thus increases proportionally to aluminium thickness in the tested packaging. Foils (Al thickness 10-42 μm) and trays (50 μm) are characterised by lower aluminium recovery yields if compared with beverage cans (90-250 μm), due to a stronger fragmentation on the combustion grate and thus the formation of smaller lumps that are lost within the fine fractions. These values also suggest that the paper used in the paper-laminated foil improves the mechanical strength of the aluminium foil.

The aluminium that is not recovered concentrates in the fine fraction of the bottom ash (< 0.8 mm), from which aluminium cannot be recovered also if advanced technologies are used. A minor amount (less than 7%) can be found in the fly ash.

Looking at the residual waste and at its natural content of aluminium, only 26-37% of the Al fed to the furnace of the incineration plant can be separated from the bottom ash with ECS technologies. This corresponds to an amount of secondary aluminium producible equal to about 21-23% of the aluminium in the URW. This value refers to the typical situation of Northern Italy, where the separated collection of waste reached 48% in 2009, with better performances in some provinces. For example, in the two provinces feeding the WTE plants where the experimentations were carried out, Lecco and Piacenza, the efficiency of the separated collection was equal to 57.3% and 50.7% in 2009, respectively, and the source separation of aluminium packaging amounted at 0.7 and 2 kg/person/year, respectively. In these situations, most of the aluminium in the residual waste probably consists of flexible packaging like the foil, and thus concentrates in the fine fraction of the bottom ash (< 0.8 mm) and cannot be recovered. Where the separated collection is less efficient, like in other Italian regions, the amount of aluminium in the residual waste can be higher and also its composition can be different, with a prevailing presence of rigid packaging materials. This may result in a greater amount of aluminium potentially recoverable from the ash.

The results previously illustrated seem to underestimate the potential for aluminium recovery from the bottom ash compared to what reported in the literature. For example, some experiences carried out in Northern Europe, especially in the Netherlands, showed that about 60-70% of the aluminium scraps can be recovered from the ash (Muchova and Rem, 2007; Manders, 2008).

Aluminium recovery from the ash is particularly difficult when the lumps produced during the combustion process are smaller than 5 mm. In fact, the standard ECS usually installed in the plant, have a good separation efficiency only for lumps bigger than 4-5 mm. The size of the lumps is related to the characteristics of the aluminium in the waste, as previously explained. For the flexible packaging, a non negligible amount of aluminium is recovered from the bottom ash fraction included between 0.8 mm and 5 mm. 21% of the recovered aluminium from the poly-laminated foil come from the lumps < 5 mm, and this amount increases to 80% when the poly-laminated foils are mixed with aluminium foils.

If we consider the residual waste, about 13-24% of the recoverable aluminium comes from the bottom ash fraction included between 0.8 and 5 mm and 76-87% from the fraction bigger than 5 mm (corresponding to 3-5% and 16-20% of the total Al in the ash, respectively). This means that, even if most of the aluminium scraps are recoverable through standard eddy current technologies, a non negligible amount of aluminium can be recovered only in advanced treatment plants.

Focusing on the fine fraction, the analysis of the bottom ash < 4 mm sampled in a Swedish plant shows that about 3% of the total aluminium, corresponding to about 21% of the metallic Al, can be recovered and recycled from the bottom ash when an advanced treatment is applied, similarly to what observed in the Italian bottom ash. The important difference that was observed between Italy and Sweden is the percentage of aluminium in the non-ferrous fraction. In the Swedish bottom ash, aluminium is only 20-30% of the total non-ferrous metals, whereas in the analysed Italian bottom ash aluminium was about 70% of the non-ferrous metals in the fraction < 5mm.
Despite the amount of aluminium detected in the Swedish bottom ash was very low, improving metal recovery from the fine fraction, by including a grinding stage and advanced ECS in the plant layout, is economical advantageous. On the contrary, the alternative of producing H_2 from the ash does not seem a good choice, especially when aluminium concentration in the ash is very low and the consequent H_2 production is modest.

Even considering all the uncertainties associated to the amount of aluminium that can be actually recovered from the bottom ash, a rough estimate of the aluminium potentially recoverable in Italy is presented in this work. The resulting values are very interesting: between 16,300 and 24,900 tonnes might be recovered in 2015 and between 19,300 and 34,600 tonnes in 2020, depending on the actual production of waste, on the separated collection and on the WTE plants that will enter into operation in the next 10 years. This corresponds to an amount of secondary aluminium potentially producible included between 11,300 and 17,300 tonnes in 2015 and between 13,400 and 24,000 tonnes in 2020. Of course, all the bottom ash should be treated, if we want to recover this amount of aluminium. This means a great improvement and development of the sector, with the construction of new bottom ash treatment plants, whose current capacity is absolutely insufficient.

6.1. FURTHER RESEARCH

The research project has focused on aluminium recovery from the bottom ash and has evaluated the amount of aluminium potentially recoverable from the ash as a function of the different packaging materials that can be present in the waste and of the scraps oxidation level.
Two main parameters influence the recovery rate:

- the type of aluminium materials that are present in the waste: types of packaging, its thickness and mechanical properties;
- the characteristics of the incineration plant and the combustion parameters: grate type, bottom ash extraction system, waste and bottom ash residence time, O_2 in the combustion chamber etc.

The experimentation involved only two incineration plants, both of them equipped with a wet discharge system of the bottom ash. The composition of the burned waste was not

analysed during the test and, thus, the actual composition of the aluminium fraction in the residual waste was unknown.
In order to complete the picture of the aluminium potentially recoverable from the bottom ash, the evaluation should be extended to other plants with different technological options (grate type, bottom ash extraction system etc). It is important to evaluate each time the waste composition in order to measure the content of the different types of aluminium materials. Once a significant data base is collected, it is possible to identify the relationship existing among the efficiency of the separated collection, the type of packaging materials present in the residual waste, the characteristic of the incineration plant, the combustion parameters and the amount of aluminium potentially recoverable from the bottom ash.

The work has also focused on aluminium recovery from the fine fraction of the bottom ash. The study was carried out only on one incineration plant and should be extended to other plants. This will allow to evaluate the amount of aluminium potentially recoverable as a function of the waste management system and of the incineration plant design and to express a more founded opinion about the alternative of H_2 production. Furthermore, if this alternative appears to be interesting, the leaching behavior of the ash after H_2 production should be investigated.

Similar investigations should be extended to other elements in the waste (like Cu, Ag, Au), in order to assess the amount of material actually recoverable from the bottom ash.

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ANNEX I

The detailed results obtained from the analysis of the samples taken during Test #7 on paper-laminated foil are here presented.

I.1. Bottom ash

Table I.1 gives an overview of the type and quantity of the sub-fractions obtained from the pre-treatment of bottom ash samples taken during Test #7 on aluminium paper-laminated foil.

Table I.1. Dry weight, humidity and sub-fractions (expressed as weight percentage on dry samples) obtained from the pre-treatment of bottom ash samples taken during Test #7 on aluminium paper-laminated foil.

Sample	**Time**	**Dry weight**	**Humidity**	**Fraction < 0.8 mm**	**Fraction < 0.8 mm (after grinding)**	**Fraction > 0.8 mm (after grinding)**	**Iron+inert scraps**
		g	***%***	***%***	***%***	***%***	***%***
BA01-1	11:20	8250	13.0	13.9	42.4	23.0	21.8
BA01-2	12:20	11450	13.9	12.2	41.3	20.1	26.9
BA01-3	13:20	9600	12.9	15.6	45.6	18.8	22.8
BA01-4	14:30	9370	21.9	21.8	42.4	18.0	18.9
BA01-5	15:00	10700	17.1	21.0	44.1	10.8	26.0
BA01-6	15:30	10180	8.3	9.4	39.9	17.8	34.2
BA01-7	16:00	9100	19.0	17.8	46.8	15.4	21.2
BA01-8	16:40	9750	17.4	15.3	31.6	17.4	36.3
BA01-9	17:25	10600	4.3	9.7	43.8	19.9	27.3
BA01-10	18:00	8480	8.9	28.0	30.8	21.2	22.1
BA01-11	18:40	9950	18.1	12.1	42.2	22.7	27.1
BA01-12	19:20	10430	10.9	21.8	39.1	15.6	21.0
BA01-13	19:50	8950	24.8	16.3	39.8	16.3	28.5
BA01-14	20:25	9520	10.2	18.7	33.1	14.7	30.7
BA01-15	20:55	9930	16.2	23.7	37.3	16.8	23.2
BA01-16	21:35	9170	5.5	12.5	45.7	9.8	33.0
BA01-17	22:00	8530	22.5	17.4	39.0	19.8	25.5
BA01-18	22:20	10880	10.8	19.7	33.1	12.3	35.8
BA01-19	22:35	10350	13.0	14.5	45.1	19.0	22.4
AVERAGE		***9747***	***14.1***	***16.9***	***40.2***	***17.4***	***26.6***
STD.DEV.		***877***	***5.7***	***4.9***	***5.0***	***3.7***	***5.3***

Fine fractions

Figures I.1 and I.2 depict the trends of total and metallic aluminium percentage content (on the dry weight) in the bottom ash fine fractions.

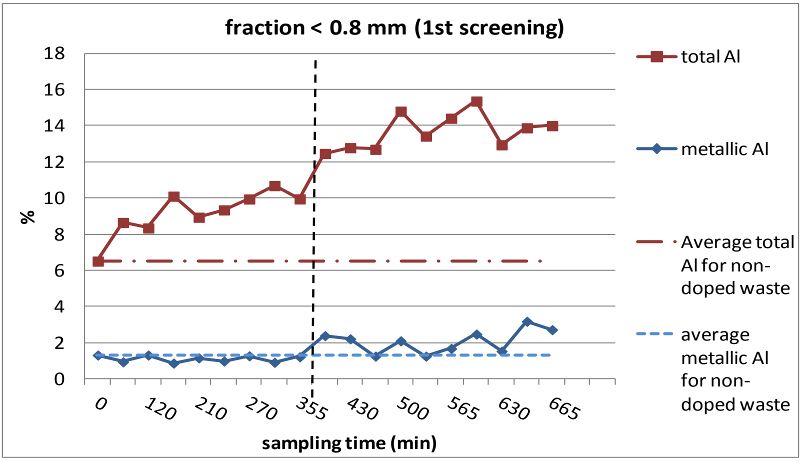

Figure I.1. Trends of total and metallic aluminium percentage content (on the dry weight) in the fraction below 0.8 mm resulting from the first screening. The vertical line indicates the beginning of the growth trend observed for these fractions.

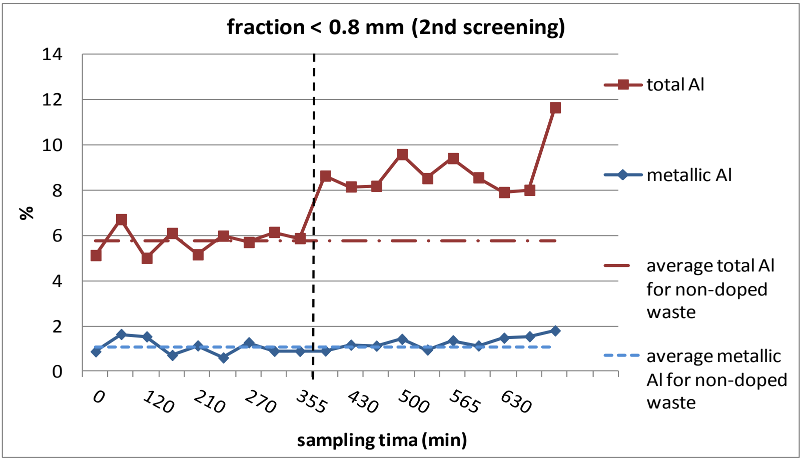

Figure I.2. Trends of total and metallic aluminium percentage content (on the dry weight) in the fraction below 0.8 mm resulting from the second screening. The vertical line indicates the beginning of the growth trend observed for these fractions.

The two fine fractions show an evident growth trend from 390 minutes after the beginning of sampling operations. This is more evident for the fine fraction after the second screening, whereas for that after the first screening total aluminium concentration seems to increase continuously from the very beginning of the sampling operations. However, the graph in Figure I.1 must not mislead. When the concentrations are rescaled on the mass on the whole bottom ash samples (before the pre-treatment of the ash), it is evident that Al concentration starts to increase from 390 minutes after the beginning of the sampling operations also for the fine fraction after the first screening, as depicted in Figure I.3.

The trend of aluminium in the fine fractions shows the impossibility to appreciate the complete evolution of the curve and, in particular, its decreasing phase towards the average values of the non-doped waste. Unfortunately the sampling time was shorter than the actual residence time of the waste in the furnace and in the bottom ash extraction system. Despite this limitation, the curves were integrated to evaluate the aluminium mass balance.

The integration of the curves of total and metallic aluminium content in the fine fractions starts from 355 minutes after the beginning of the sampling.

Dotted horizontal lines indicate the average values of total and metallic aluminium percentage content calculated for the non-doped waste. Concerning the fine fraction resulting from the first screening, the average total aluminium content is equal to 9.2%, while the average metallic aluminium content is 1.1%. For the fine fraction resulting from the second screening, the average percentage contents are equal to 5.8% and 1.1%, respectively.

Table I.2 reports the calculation of fed packaging average contribution. Table I.3 shows the aluminium content in the metallic form in the two bottom ash fine fractions. Less than 29% of the aluminium in the fine fractions is present in the metallic form. The table does not reveal any significant change due to the doping of the waste.

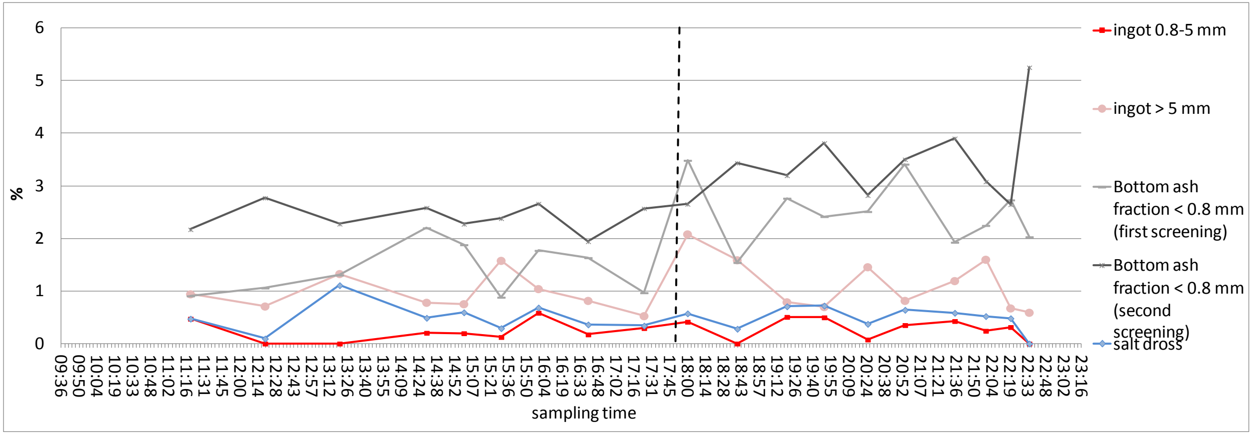

Figure I.3. Temporal evolution of total Aluminium concentration in the bottom ash samples during the tests on aluminium paper-laminated foil. Percentage is expressed on the mass of the total bottom ash samples. The vertical line indicates the beginning of the growth trend observed for these fractions.

Table I.2. Calculation of fed packaging average contribution in the bottom ash fine fractions resulting from the first and second screening.

	Fraction < 0.8 mm (1st screening)		**Fraction < 0.8 mm (2nd screening)**	
	Metallic Al	**Total Al**	**Metallic Al**	**Total Al**
A1	0.63	3.92	0.31	2.54
A2	0.92	5.05	0.41	3.36
A3	0.69	5.10	0.45	3.27
A4	0.50	4.13	0.38	2.66
A5	0.59	4.94	0.41	3.17
A6	0.44	4.18	0.34	2.69
A7	0.83	5.96	0.49	3.59
A8	0.50	3.54	0.32	2.06
A9	0.47	2.68	0.30	1.59
A10	0.44	2.09	0.25	1.47
Doped waste contribution (kg_{Al} $kg^{-1}_{bottom\ ash}$ min)	6.01	41.59	3.68	26.39
Non-doped waste contribution (kg_{Al} $kg^{-1}_{bottom\ ash}$ min)	3.42	28.41	3.26	17.83
Contribution of fed packaging (kg_{Al} $kg^{-1}_{bottom\ ash}$ min)	**2.58**	**13.18**	**0.42**	**8.57**

Table I.3. Aluminium content in the metallic form in the bottom ash fine fractions resulting from the first and second screening.

	Metallic Al/Total Al (%)	
Sample	**Fraction < 0.8 mm (1st screening)**	**Fraction < 0.8 mm (2nd screening)**
BA01-1	20.1	16.9
BA01-2	10.8	24.3
BA01-3	15.7	30.5
BA01-4	8.6	11.5
BA01-5	12.9	21.9
BA01-6	10.5	9.9
BA01-7	12.7	22.2
BA01-8	8.5	14.4
BA01-9	12.2	15.1
BA01-10	19.1	10.4
BA01-11	17.3	14.2
BA01-12	9.8	13.6
BA01-13	14.2	14.8
BA01-14	9.3	11.1
BA01-15	11.6	14.4
BA01-16	16.1	13.1
BA01-17	11.8	18.5
BA01-18	22.9	19.1
BA01-19	19.4	15.6
AVERAGE	***13.9***	***16.4***
STD.DEV.	***4.3***	***5.3***

Ingot fraction

Table I.4 shows the yields (%) obtained from non-ferrous metals melting process, expressed as the ratio between the weight of the metal ingot resulting from melting in the crucible and the total dry weight of the corresponding bottom ash sample. Data are reported separately for the ingot obtained from the non-ferrous fraction 0.8-5 mm and the one obtained from the non-ferrous fraction bigger than 5 mm. Their sum can be regarded as the maximum total efficiency of an advanced bottom ash treatment plant for the recovery of non-ferrous metals.

Table I.4. Yields (%) obtained from non-ferrous metals melting processes.

Sample	**Yield of non-ferrous metals 0.8-5 mm**	**Yield of non-ferrous metals > 5 mm**
	w% (ingot 0.8-5 mm/dry BA sample)	w% (ingot > 5 mm/dry BA sample)
BA01-1	0.7	1.1
BA01-2	0.0	0.9
BA01-3	0.0	1.6
BA01-4	0.3	1.0
BA01-5	0.3	0.9
BA01-6	0.2	1.7
BA01-7	0.9	1.3
BA01-8	0.3	1.0
BA01-9	0.5	0.7
BA01-10	0.6	2.2
BA01-11	0.0	1.9
BA01-12	0.7	1.0
BA01-13	0.7	0.8
BA01-14	0.1	1.8
BA01-15	0.5	0.9
BA01-16	0.5	1.3
BA01-17	0.3	1.8
BA01-18	0.5	0.8
BA01-19	0.3	0.9
AVERAGE	***0.4***	***1.2***
STD.DEV.	***0.3***	***0.5***

Figure I.4 shows the trend of metallic aluminium percentage content in the ingots resulting from the melting process. Data were obtained by multiplying the non-ferrous metals yield for each sample by the metallic aluminium concentration given by the OES analysis on the ingots. The percentage content is therefore representative of the actual amount of aluminium recoverable from each bottom ash sample.

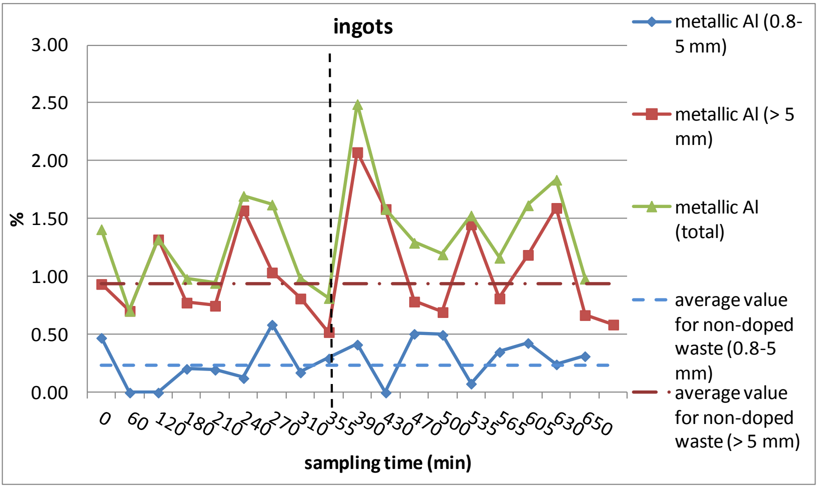

Figure I.4. Trend of metallic aluminium percentage content (on the dry weight) in the ingots resulting from the melting process of the 0.8 - 5 mm and > 5 mm sub-fractions. The vertical line indicates the beginning of the observed growth trend, also taking into account the growth trend observed in the fine fractions.

The percentage content of metallic aluminium in the ingots presents an irregular trend, and no clear increase linked to the doping of the waste can be observed.

Table I.5 reports the total recovery of metallic aluminium from the two coarse sub-fractions (expressed as a percentage on the dry weight of the initial bottom ash sample) and the corresponding contribution of the 0.8 - 5 mm sub-fraction. On average, about 20% of the aluminium recovered as an ingot comes from the fraction 0.8-5 mm, with a variability quite important. In fact in some samples, the aluminium recovered from the fraction smaller than 5 mm is about 40% of the whole recovered aluminium.

It is important to keep in mind that these values include the background aluminium concentration of the non-doped waste, so they do not correspond to the sole fed packaging contribution of the 0.8 - 5 mm sub-fraction.

Table I.5. Total recovery of metallic aluminium from the two coarse sub-fractions and contribution of the 0.8-5 mm sub-fraction. Samples representative of the doped waste are highlighted in italics.

Sample	**Total recovery of metallic Al**	**Contribution of 0.8 - 5 mm sub-fraction**
	w% (referred to dry BA sample)	w% (referred to metallic Al in the ingot)
BA01-1	1.4	33.5
BA01-2	0.7	0.0*
BA01-3	1.3	0.0*
BA01-4	1.0	20.8
BA01-5	1.0	20.8
BA01-6	1.7	7.3
BA01-7	1.6	36.1
BA01-8	1.0	17.6
BA01-9	0.8	36.0
BA01-10	*2.5*	*16.6*
BA01-11	*1.6*	*0.0**
BA01-12	*1.3*	*39.2*
BA01-13	*1.2*	*41.8*
BA01-14	*1.5*	*5.0*
BA01-15	*1.2*	*30.1*
BA01-16	*1.6*	*26.5*
BA01-17	*1.8*	*13.2*
BA01-18	*1.0*	*31.9*
BA01-19	*0.6*	*n.a.***
AVERAGE	***1.3***	***19.8***
STD.DEV.	***0.5***	***14.7***

*The 0.8 - 5 mm sub-fraction did not contain recoverable aluminium so its contribution is equal to zero.

**the ingot resulting from the melting process was too little to be analysed.

Considering aluminium growth trend in the fine fractions of the bottom ash and assuming that the behaviour of the fraction above 0.8 mm (i.e. the ingot fraction) is equal to that of the two fine fractions, the beginning of the effects of the doped waste can be set at 18:00, 390 minutes after the beginning of the bottom ash sampling.

As the first charge of doped waste was introduced in the feeding hopper at 8:30, 170 minutes before the start of sampling operations, the estimated residence time is approximately equal to 9 hours and 20 minutes.

The integration of the two curves was calculated starting from 355 minutes after the beginning of the sampling to the end of the sampling period, resulting in an integration interval of 310 minutes. Table I.6 summarises the results of the calculation for both the coarse sub-fractions.

Table I.6. Calculation of fed packaging average contribution in the ingots.

Area	Sub-fraction 0.8 - 5 mm	Sub-fraction >5 mm	Total
A1	0.25	0.91	1.16
A2	0.17	1.47	1.63
A3	0.20	0.95	1.15
A4	0.30	0.44	0.75
A5	0.20	0.75	0.95
A6	0.13	0.68	0.81
A7	0.31	0.80	1.11
A8	0.17	0.70	0.86
A9	0.11	0.45	0.56
A10	0.05	0.19	0.24
Doped waste contribution (kg_{Al} $kg^{-1}_{bottom\ ash}$ min)	1.89	7.34	9.23
Non-doped waste contribution (kg_{Al} $kg^{-1}_{bottom\ ash}$ min)	0.71	2.91	3.62
Contribution of fed packaging (kg_{Al} $kg^{-1}_{bottom\ ash}$ min)	**1.18**	**4.43**	**5.61**

Results of the analysis on the salt dross from the melting process of the 0.8 - 5 mm sub-fraction are reported in Figure I.5. For the sub-fraction above 5 mm, no dross has been produced since it consisted of non-ferrous lumps (from preliminary sorting and 5 mm mesh screening) nearly without any impurity. Percentages refer to the total dry weight of bottom ash samples, as usual.

For the first sample, the analysis of the salt dross was not possible due to technical problems. The high concentration of

Al in the third sample is attributable to technical problems in the melting process. By excluding this value, no clear growth trend linked to the doping of the waste can be observed. About 70% of the aluminium in the salt dross is present in its oxidised form, whereas the loss of metallic Al in the crucible is quite modest, as illustrated in Table I.7.

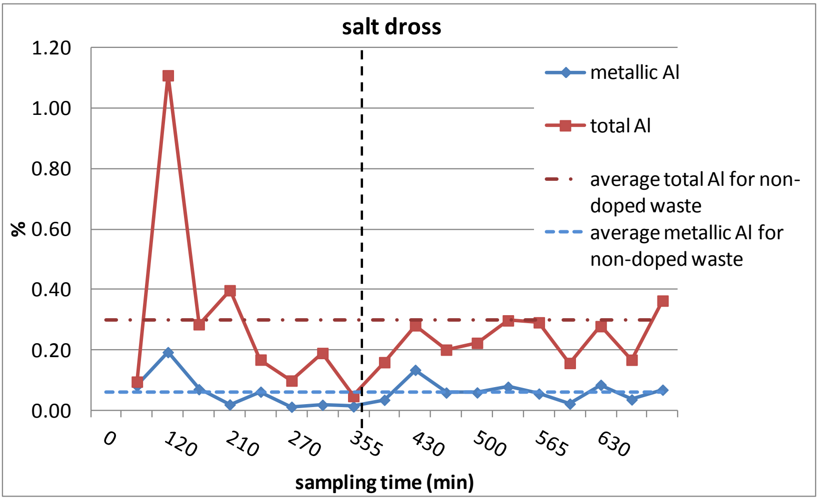

Figure I.5. Aluminium percentage content (on the dry weight) in the salt dross resulting from the melting process of the 0.8 - 5 mm sub-fraction.

Table I.7. Loss of metallic aluminium during the melting process in the crucible. Samples representative of the doped waste are highlighted in italics.

Sample	**Metallic Al (%) in the fraction > 0.8 mm**	**Loss of metallic Al in the crucible (%)**
SD1-1	n.a.	n.a.
SD1-2	0.8	10.3
SD1-3	1.5	12.7
SD1-4	1.1	6.6
SD1-5	1.0	2.0
SD1-6	1.8	3.5
SD1-7	1.6	0.7
SD1-8	1.0	1.8
SD1-9	0.8	1.5
SD1-10	*2.5*	*1.4*
SD1-11	*1.7*	*7.8*
SD1-12	*1.4*	*4.3*
SD1-13	*1.3*	*4.7*
SD1-14	*1.6*	*4.8*
SD1-15	*1.2*	*4.5*
SD1-16	*1.6*	*1.3*
SD1-17	*1.9*	*4.4*
SD1-18	*1.0*	*3.5*
SD1-19	*0.7*	*10.4*
AVERAGE	**1.4**	**4.5**
STD.DEV.	**0.5**	**3.6**

The contribution of the paper-laminated foils to the aluminium concentration in the salt dross was evaluated assuming the same integration interval as for the ingots. Results are reported in Table I.8.

Table I.8. Calculation of fed packaging average contribution in the salt dross.

Area	**Metallic Al**	**Total Al**
A1	0.02	0.07
A2	0.07	0.18
A3	0.08	0.19
A4	0.04	0.13
A5	0.05	0.18
A6	0.04	0.18
A7	0.03	0.18
A8	0.03	0.11
A9	0.02	0.09
A10	0.02	0.08
Doped waste contribution (kg_{Al} $kg^{-1}_{bottom\ ash}$ min)	0.38	1.38
Non-doped waste contribution (kg_{Al} $kg^{-1}_{bottom\ ash}$ min)	0.18	0.93
Contribution of fed packaging (kg_{Al} $kg^{-1}_{bottom\ ash}$ min)	**0.20**	**0.46**

I.2. Fly ash

Boiler ash

Figure I.6 shows the percentage content of total and metallic aluminium measured in boiler ash samples.

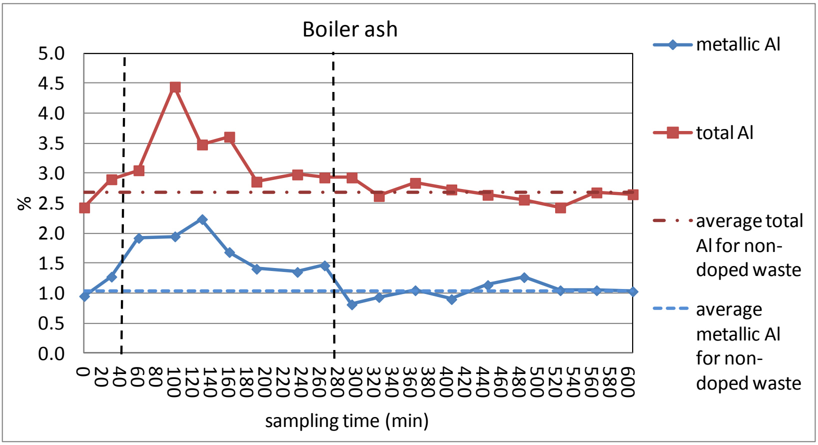

Figure I.6. Percentage content of total and metallic aluminium measured in boiler ash samples. The integration interval used in the calculation of fed packaging average contribution is delimited by vertical dotted lines.

The growth trend appears around 60 minutes after the start of the sampling. Considering that the first charge of doped waste was introduced into the furnace at 8:30 and boiler ash sampling started at 9:15, the estimate of the response time amounts to 105 minutes. The integration interval, identified by vertical dotted lines, is equal to 365 minutes and corresponds to the period during which boiler ash samples representative of the doped waste were taken. Table I.9 shows the results of the numerical integration, carried out in the usual way.

Table I.9. Calculation of fed packaging average contribution in boiler ash.

Area	Metallic Al	Total Al
A1	0.48	0.89
A2	0.77	1.50
A3	0.63	1.19
A4	0.59	1.06
A5	0.46	0.97
A6	0.62	1.31
A7	0.42	0.89
A8	0.34	0.88
Doped waste contribution ($kg_{Al}\ kg^{-1}_{boiler\ ash}$ min)	4.32	8.69
Non-doped waste contribution ($kg_{Al}\ kg^{-1}_{boiler\ ash}$ min)	2.76	7.09
Contribution of fed packaging ($kg_{Al}\ kg^{-1}_{boiler\ ash}$ min)	**1.56**	**1.61**

ESP ash

Figure I.7 shows the percentage content of total and metallic aluminium measured in ESP ash samples.

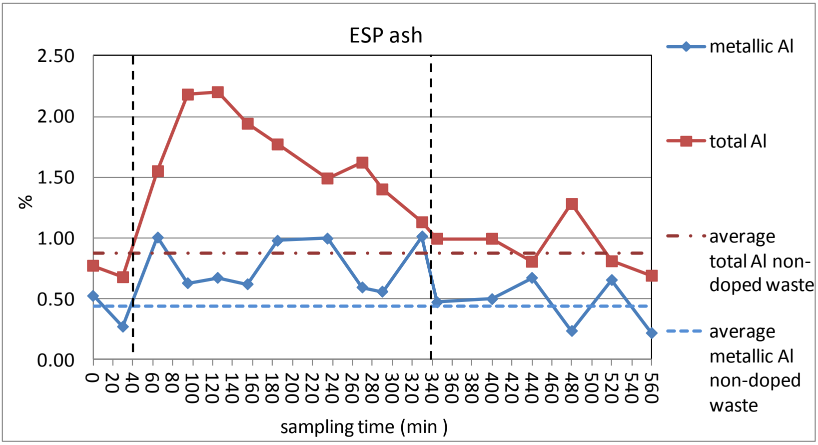

Figure I.7. Percentage content of total and metallic aluminium measured in ESP ash samples. The integration interval used in the calculation of fed packaging average contribution is delimited by vertical dotted lines.

The growth trend appears around 65 minutes after the start of the sampling. Considering that the first charge of doped waste was introduced into the furnace at 8:30 and ESP ash sampling started at 9:20, the estimate of the response time amounts to 115 minutes. The integration interval, identified by vertical dotted lines, is equal to 315 minutes and corresponds to the period during which ESP ash samples representative of the doped waste were taken. Table I.10 shows the results of the numerical integration, carried out in the usual way.

Table I.10. Calculation of fed packaging average contribution in ESP ash.

Area	Metallic Al	Total Al
A1	0.22	0.39
A2	0.24	0.56
A3	0.20	0.66
A4	0.19	0.62
A5	0.24	0.56
A6	0.49	0.82
A7	0.28	0.54
A8	0.12	0.30
A9	0.31	0.51
A10	0.11	0.16
Doped waste contribution (kg_{Al} $kg^{-1}_{ESP\ ash}$ min)	2.41	5.11
Non-doped waste contribution (kg_{Al} $kg^{-1}_{ESP\ ash}$ min)	1.40	2.76
Contribution of fed packaging (kg_{Al} $kg^{-1}_{ESP\ ash}$ min)	**1.01**	**2.35**

FF ash

Figure I.8 shows the percentage content of total and metallic aluminium measured in FF ash samples.

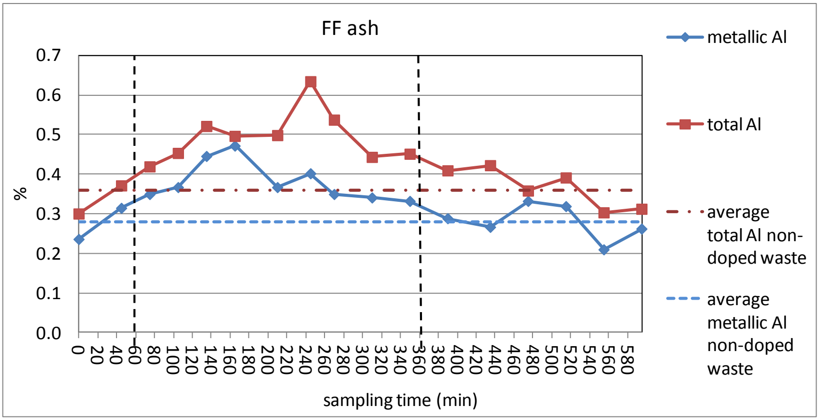

Figure I.8. Percentage content of total and metallic aluminium measured in FF ash samples. The integration interval used in the calculation of fed packaging average contribution is delimited by vertical dotted lines.

The growth trend appears around 75 minutes after the start of the sampling. Considering that the first charge of doped waste was introduced into the furnace at 8:30 and FF ash sampling started at 9:30, the estimate of the response time amounts to 135 minutes. The integration interval, identified by vertical dotted lines, is equal to 345 minutes and corresponds to the period during which FF ash samples representative of the doped waste were taken. Table I.11 shows the results of the numerical integration, carried out in the usual way.

Table I.11. Calculation of fed packaging average contribution in FF ash.

Area	Metallic Al	Total Al
A1	0.10	0.12
A2	0.11	0.13
A3	0.12	0.15
A4	0.14	0.15
A5	0.19	0.22
A6	0.13	0.20
A7	0.09	0.15
A8	0.14	0.20
A9	0.13	0.18
A10	0.12	0.17
Doped waste contribution (kg_{Al} $kg^{-1}_{FF\ ash}$ min)	1.16	1.49
Non-doped waste contribution (kg_{Al} $kg^{-1}_{FF\ ash}$ min)	0.96	1.24
Contribution of fed packaging (kg_{Al} $kg^{-1}_{FF\ ash}$ min)	**0.20**	**0.25**

I.3.Bottom ash quenching water

During this test, only two samples of bottom ash quenching water were taken, due to technical problems. Both samples referred to the non-doped waste, as reported in table I.12. For this reason, the contribution of aluminium foil to aluminium concentration in the quenching waste could not be evaluated.

Table I.12. Total aluminium concentration in the bottom ash quenching water.

Sample	time	Total Al (mg l^{-1})
W1-1	14:30	1130
W1-2	16:30	797

I.4. Mass balance

Table I.13 lists all the flow rates considered in the calculation of the final mass balance.

Table I.13. Waste and residues flow rates used in the calculation of the final mass balance for aluminium paper-laminated foils.

	Flow rate (kg h^{-1})	**Flow rate (w% on waste flow rate)**
Waste	5076	100
Boiler ash	82	1.6
ESP ash	105	2.1
FF ash	41	0.8
Dry bottom ash	830	16.4
Bottom ash fraction < 0.8 mm (1st screening)	140	2.8
Bottom ash fraction < 0.8 mm (2nd screening)	333	6.6
Bottom ash quenching tank	3.1*	-

*m^3

Table I.14 shows the results of the final mass balance, obtained by multiplying the fed packaging average contribution in each fraction by the corresponding flow rate converted to kg min^{-1}. The actual amount of pure aluminium fed to the furnace (358 kg) is significantly lower than the amount of fed packaging (635 kg). The packaging introduced into the furnace consists, in fact, of a 12 µm thick aluminium foil poly-laminated with 25 g m^{-2} of paper. The determination of the aluminium amount introduced with paper-laminated foils required thus the consideration of their specific structure and composition.

Table I.14. Mass balance related to Test #7 on paper-laminated foils.

	Total Al (kg)	**Partitioning of recovered total Al in the residues (%)**	**Metallic Al (kg)**	**Metallic/ Total Al (%)**
INPUT				
Fed aluminium	358		358	
OUTPUT				
Boiler ash	2.2	1.3	2.1	96.9
ESP ash	4.1	2.4	1.8	43.2
FF ash	0.2	0.1	0.1	76.7
Bottom ash fraction < 0.8 mm before grinding	30.9	18.3	6.1	19.6
Bottom ash fraction < 0.8 mm after grinding	47.6	28.2	2.3	4.9
Ingots from 0.8 - 5 mm sub-fraction	16.3	9.7	16.3	100.0
Ingots from > 5 mm sub-fraction	61.4	36.3	61.4	100.0
Salt dross	6.3	3.8	2.8	43.6
Bottom ash quenching water	n.a.		n.a.	
Total recovered aluminium	168.9		92.8	55.0

The mass balance shows that about 47% of the aluminium introduced into the furnace has been recovered in the incineration residues (169 out of 358 kg), due to the short sampling time. Excluding fly ash (that accounts for less than 4% of the total Al), aluminium was recovered half in the fine fractions and half as ingots. The amount of aluminium actually recoverable as ingots is therefore very interesting, especially considering the extremely thin structure of the tested packaging.

79% of the recovered aluminium comes from the >5 mm fraction whereas only 21% of the lumps were recovered from the 0.8-5 mm fraction. This suggest that a relevant part of paper-laminated foil can be recovered in standard bottom ash treatment plant. In any case, adding an advanced ECS specifically calibrated on grains smaller than 5 mm allows to increase the yield of aluminium recovery by a non negligible 27%.

4% of the paper-laminated foil fed to the furnace is lost during the melting process in the salt dross and almost half of this amount is in the metallic form. However, we must take in account the differences between the melting process in the melting pot, performed during the experimentation, and the real recycling process in the secondary smelter. In addition, foundries usually treat the salt dross in order to further recover the metallic aluminium trapped in the salt.

Only 55% of the recovered aluminium is in its metallic form, as expected considering the thin structure of the packaging and, consequently, the potentially high oxidation level of aluminium. In particular, the metallic/total Al ratio is particularly low for the bottom ash fine fractions whereas, on the contrary, most of the aluminium in the fly ash is metallic.

The complete mass balance of aluminium can be tentatively estimated by enlarging the integration interval of the bottom ash. An integration interval twice the one previously used for the bottom ash was assumed, based on two considerations:

- Bottom ash (ingots and fine fraction after the second screening) resulting from the doped waste was sampled for about 5 hours, without observing a decreasing of aluminium concentration. We can assume that only the first half of the curve was measured and, thus, the time frame interested by the extraction of the doped bottom ash was double the integration time reported in chapter I.1.
- The interval between the time when the first sample of doped bottom ash was observed during the test #6 and the start of the test #7 was equal to 13 hours. Thus, the

period of time interested by the extraction of the doped bottom ash must be shorter than 13 hours.

Of course this is only a hypothesis and the obtained values must be considered as a rough indication.

Based on the previous considerations, the mass balance of the paper-laminated foil was calculated by doubling the amount of aluminium recovered from the bottom ash, the ingot fraction and the salt dross. The results are reported in Table I.15.

Table I.15. Theoretical mass balance related to Test #7 on paper-laminated foils, evaluated by double the amount of aluminium recovered from the bottom ash.

	Total Al (kg)	**Partitioning of recovered total Al in the residues (%)**	**Metallic Al (kg)**	**Metallic/ Total Al (%)**
INPUT				
Fed aluminium	358		358	
OUTPUT				
Boiler ash	2.2	0.7	2.1	96.9
ESP ash	4.1	1.2	1.8	43.2
FF ash	0.2	0.1	0.1	76.7
Bottom ash fraction < 0.8 mm before grinding	61.7	18.6	12.1	19.6
Bottom ash fraction < 0.8 mm after grinding	95.2	28.7	4.6	4.9
Ingots from 0.8 - 5 mm sub-fraction	32.6	9.9	32.6	100.0
Ingots from > 5 mm sub-fraction	122.7	37.0	122.7	100.0
Salt dross	12.7	3.8	5.5	43.6
Bottom ash quenching water	n.a.	n.a.	n.a.	n.a.
Total recovered aluminium	331.4		181.6	54.8

By doubling the integration interval of the bottom ash, the total amount of aluminium recovered in the residues results 92.5% of the aluminium introduced in the furnace.

Comparing the results of the two mass balances (the real one and the estimated one), a fraction of total aluminium included between 96 and 98% concentrates in the bottom ash (fine fractions plus ingots), with only a negligible quantity that is lost with fly ash.

About 46-47% of the total aluminium fed into the furnace can be actually recovered from the bottom ash and recycled. Nearly one fifth of this amount comes from smaller lumps (ingot 0.8-5 mm), which means it is recoverable only if advanced treatments for the bottom ash are applied. The residual amount of total aluminium (46-47% of the aluminium fed to the furnace) concentrates in the fine fractions of the bottom ash and, thus, cannot be recovered with the current ECS technologies.

About 4% of the total aluminium theoretically recoverable is lost during the melting process and concentrates in the dross salt.